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AN EXPERIMENTAL STUDY OF THE WASTE FIELD OF DYNAMOS.[1]

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IN 1886 a remarkable paper was published by Drs. John and Edward Hopkinson concerning the magnetic circuit of certain types of dynamos. In this paper were given some measurements of the quantity called "v," or the ratio of the total flux of force in the field magnet to that in the armature; this was found to be about 1.32.

The method used was the ballistic galvanometer one of measuring induction through a closed magnetic circuit, the dynamo magnet being so regarded. Turns of wire were placed around the field coils, armature, and other parts of the machine, as well as in the air about the magnet. The published report states that the magnets were alternately excited and short circuited; the terminals of the secondary coils were connected in turn to a reflecting galvanometer with a weighted needle.

In a paper read before the Institution of Electrical Engineers in February, 1890, Mr. W. B. Esson gave a table of values of "v" for different dynamos. This table will be quoted later in the paper. At my suggestion, Messrs. Brown and Greenlaw decided to make an extended and careful set of tests on a number of forms of dynamo magnets which were in the dynamo room of the Physical Department. After a few experimental trials, the apparatus and circuits were

[1] I have embodied in this paper the results of the graduating thesis of Messrs. Edward D. Brown and Frank M. Greenlaw, of the class of 1890, Massachusetts Institute of Technology, together with some of my own measurements made in the winter of 1887–88.

arranged in the following manner: All observations were taken in a basement room remote from the electrical and mechanical disturbances of the dynamos. A Hartmann galvanometer was set up, with a wooden block substituted for the copper one in which the bell-magnet is usually placed. The coils used with the instrument were of about 356 ohms, connected in series; an adjustable resistance was used to control the extent of the deflection without change of adjustment of galvanometer coils. This resistance was kept constant during a test. The deflections were read by a telescope and scale. A few turns of wire were wound over the regular coils and put in circuit with a suitable resistance, a cell of battery and reversing key, to enable the observer to quickly bring the needle to rest after a deflection had been received.

Exploring coils were wound upon different parts of the dynamo to be tested, the number of turns of each coil was chosen so that the deflections of the ballistic galvanometer should in all cases be as nearly alike as convenient. A mercury-cup switch-board was arranged with a set of cups for the terminals of each coil, and an ebonite block with two pins in it was arranged with flexible twisted wires, so that the galvanometer could be quickly connected to any one of the exploring coils.

The dynamo experimented upon was necessarily at rest, and the fields excited by another machine; the current in the magnet coils was of the strength it should be if the machine were running properly at no load. Of course the values of "v" thus obtained are not correct for the machine when running either at partial or full load.

The method of conducting the experiments was for the observer at the galvanometer to signal by telegraph to the operator at the dynamo his readiness to receive a deflection, at which the field circuit was closed; on again receiving a signal the circuit was opened. The same readings were then taken with the galvanometer commutator reversed, and in turn the procedure was repeated for all the coils upon the machine. Several series of deflections were taken at each time of experimenting, and from these means the results were calculated.

The Edison dynamo was first chosen on account of the simplicity of its construction. It is rated as a No. 4 dynamo, having a capacity of 150 110 volt, 16 candle-power, incandescent lamps, and as the lamps

furnished with the dynamo average about 50 watts each, this is equivalent to rating the machine at 7,500 watts; but as the ammeter is marked full load at 80 ampères corresponding to 8,800 watts, the exact rating is doubtful. The dynamo will give an output of 90 ampères all day and run cool and give no trouble.

DIMENSIONS.

Taken from a blue print.

Wrought-iron magnet cores . . .	7⅞ inches in diameter, 12⅛ inches long.
Wrought-iron yoke	10⅛ inches long, 5⅛ inches wide and thick.
Cast-iron pole pieces	12 inches long, 7⅞ inches high.
Clearance	$\frac{1}{16}$ inch.
Horns of pole pieces	2¾ inches apart.
Armature core washers	6¼ inches in diameter, with 2⅜ inch hole.
Armature core	12 inches long, 6¼ inches in diameter.
Revolutions per minute	1520.

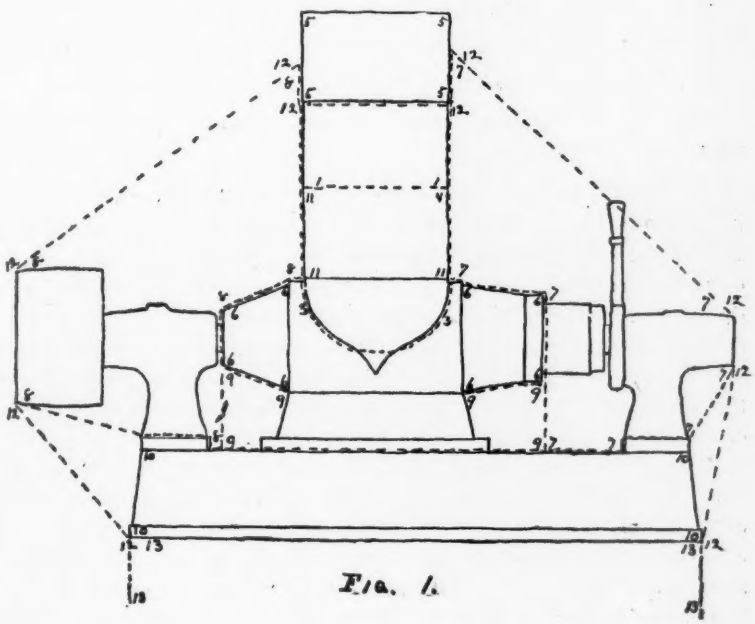


FIG. 1.

Figure 1 will show better than words the position of the various exploring coils which will be named as follows:

EXPLORING COILS.

Coil.	Turns.	Position.
1	1	Middle of magnet spool.
2	1	Middle of magnet spool.
3	1	Pole piece.
4	1	Pole piece.
5	1	Middle of yoke.
6	1	Armature, including heads.
7	6	Space, including commutator and bearing.
8	6	Space, including pulley and bearing.
9	10	Space between armature and iron base.
10	5	Iron bed-plate.
11	12	Between magnet coils from armature to plane of 1 and 2.
12	1	Whole machine and bed-plate, except yoke.
13	5	Under bed-plate to a depth of about 14 inches.

Two methods were used to produce the magnetization and demagnetization of the machine, which I will call the first method and the second method respectively. In the first method the field magnet circuit was completed and broken by means of the main switch of the dynamo. A considerable arc was formed upon breaking, which was at first reduced by connecting the pilot lamp across the magnet terminals; but as this reduced the deflection, its use was given up and the arc allowed to burn. This method is objectionable on account of the great strain the insulation of the wire has to stand, and would not be safe to use on high voltage machines. The second method was devised to put less strain on the insulation, as well as to find what the difference would be between it and the first method. The magnet was connected in series with a suitable resistance to mains of higher voltage (180 volts), and a snap-switch arranged to demagnetize the machine by short-circuiting it, and to magnetize it when the short circuit was opened. This method worked very well and was perfectly satisfactory

in every way. It was found that when the machine was magnetized, these methods gave practically the same results, both in the value of the deflections and in the percentage distribution of the lines of force; but when the machine was demagnetized, the deflections of the first method were slightly more than twice as great as in the second, although the percentage values were not so widely different.

The table shows the mean percentage distribution of the magnetization as found by both the first and second methods, and also the mean of these; one hundred per cent. represents the mean value of the magnetization of the field coils.

EDISON INCANDESCENT DYNAMO.

Percentage Distribution of Magnetization.

Coil.	Position of Coil.	First Method.		Second Method.		Average.	
		Mag.	Demag.	Mag.	Demag.	Mag.	Demag.
1 & 2	Middle of magnetizing coils . . .	100.	100.	100.	100.	100.	100.
3 & 4	Pole pieces	86.8	84.0	86.0	83.1	86.4	83.6
5	Middle of yoke	98.3	96.3	96.5	97.3	97.4	96.8
6	Armature, including heads . . .	65.8	63.5	64.8	63.7	65.3	63.6
7	Space, including commutator and bearing	2.3	2.3	2.6	2.6	2.5	2.5
8	Space, including pulley and bearing .	2.9	3.0	2.9	3.3	2.9	3.2
9	Space between armature and bed-plate	3.8	3.6	3.8	3.7	3.8	3.7
10	Iron bed-plate	9.3	8.8	9.2	8.3	9.3	8.6
11	Between magnet coils	5.6	6.0	5.6	6.4	5.6	6.2
12	Whole machine and bed, except yoke	—	—	90.1	90.5	—	—
13	Wood frame under bed-plate . . .	—	—	2.6	2.9	—	—
	The value of "v" is	1.52	1.57	1.54	1.57	1.53	1.57

I am not able to satisfactorily explain the cause of variation between the two methods or between the makes and breaks, but I am inclined to think it is due mostly to the fact that the ballistic method assumes

one condition which cannot hold with large magnetic circuits, and that is that the needle receives the impulse before it has moved appreciably. Probably these discrepancies would not be observed if a galvanometer should be made with a specially constructed needle of great mass, built up of thin laminæ so arranged that the poles of the magnetic system would not be altered by the current in the coils of the instrument.

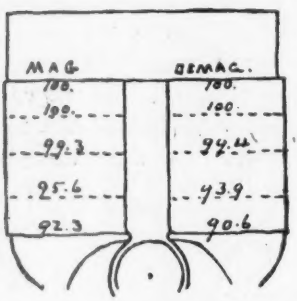


Fig. 2.

The leakage along the magnet limbs is shown by Fig. 2, which gives the positions in which the exploring coil was placed, and the values obtained.

THOMSON-HOUSTON INCANDESCENT DYNAMO.

This dynamo is of very peculiar design, being in the main an adaptation of the well-known Thomson-Houston arc-light pattern to an incandescent machine. The spherical armature revolves between the cup-shaped ends of two horizontal cylindrical cores, each of which has a heavy flange on its outer end. These flanges are connected by sixteen two-inch wrought-iron bars, as well as by two heavy cast-iron side brackets which support the main bearings of the armature shaft, and have downward projections to serve as the four legs upon which the machine stands.

As there is very little external evidence of magnetism when the dynamo is running, and the yoke bars and brackets are in effect a closed cylindrical iron shell, with its axis concentric with the axis of the magnet cores, preliminary examination was made with a small compass, and the general direction of the leakage determined. These leakage lines were substantially like those given in Hering's "Principles of Dynamo Electric Machinery."

Strong consequent points were found in the yoke bars, and a number of trials had to be made before a satisfactory set of exploring coils could be arranged. This dynamo was presented to the Physical Department with the understanding that its rating was 9,600 watts at a speed of 1,250 revolutions per minute, and a voltage of 110; but the same size

machine was listed as a 200 light dynamo with an output of 12,600 watts. It will easily run all day delivering 150 ampères at 110 volts, or 16,500 watts, without any undue heating or trouble of any kind. Exploring coils were arranged as shown in Fig. 3.

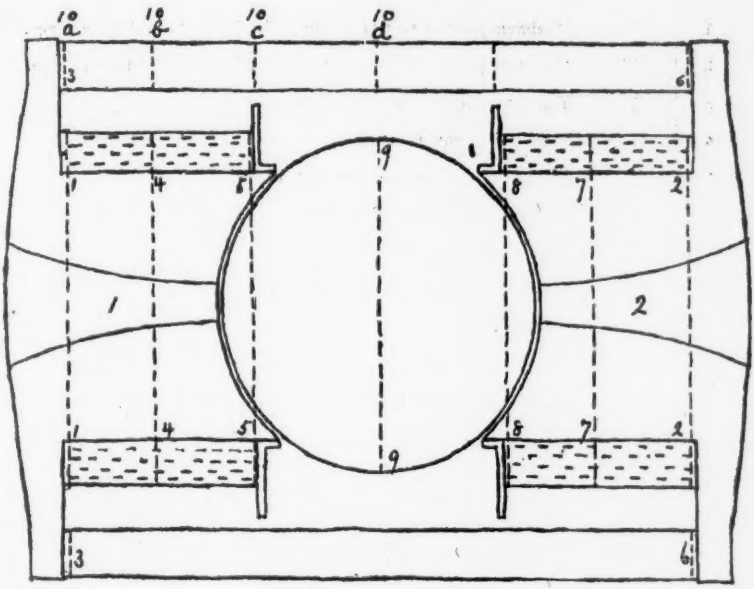


FIG. 3.

A small compass was used in determining the proper positions for these coils; very little magnetism was evident outside of the machine, but there was a very strong field between the poles and the yoke bars. The method of making and breaking the field circuit was alone employed on this dynamo, as well as on all other machines tested.

The table shows the percentage distribution of the magnetization as found both by magnetizing and demagnetizing. Coil 2 is lower than 1, and 8 than 5, probably because of the German silver turns which were short-circuited for regulation of potential of the dynamo; in this machine the resistance is wound on the machine itself and cut out when necessary by suitable screws and slides on the top of the magnet spools.

EXPLORING COILS.

Coil.	Turns.	Position.
1	1	Maximum position on magnet spool No. 1, about ½ inch from flange.
2	1	Maximum position on magnet spool No. 2, about ½ inch from flange.
3	1	Yoke bars and brackets No. 1.
4	1	Middle of magnet spool No. 1.
5	1	Armature end of magnet spool No. 1.
6	1	Yoke bars and brackets No. 2.
7	1	Middle of magnet spool No. 2.
8	1	Armature end of magnet spool No. 2.
9	1	Armature.
10	5	Moveable coils around one group of 4 yoke bars.
11	5	End of yoke bracket. Commutator side. Plane of 10 a.
12	6	Yoke bracket opposite magnetic pole. Commutator side. Plane of 10 c.
13	6	End of yoke bracket. Pulley side. Plane of 10 a.
14	6	Yoke bracket opposite magnet pole. Pulley side. Plane of 10 c.
15	6	Middle of yoke bracket. Pulley side. Plane of 10 d.

Although these results are of value in the study of dynamo magnets, it must be remembered that this machine was at rest, and there was no current in the armature or series winding. The series turns are placed over the armature and at such a fixed inclination as to tend to neutralize the cross magnetization of the armature, rendering the frequent adjustment of the brushes unnecessary. These series coils are very powerful and must make a very decided difference in the distribution of magnetism.

THOMSON–HOUSTON INCANDESCENT DYNAMO.

Percentage Distribution of Magnetization.

Coil.	Position of Coil.	Mag.	Demag.
1	Maximum position, spool No. 1	100.0	100.0
2	Maximum position, spool No. 2	98.7	99.1
3	Yoke bars and brackets No. 1	94.3	93.5
4	Middle of spool No. 1	95.5	96.6
5	Armature end of spool No. 1	81.5	82.5
6	Yoke bars and brackets No. 2	93.5	92.2
7	Middle of spool No. 2	95.3	96.2
8	Armature end of spool No. 2	80.3	79.9
9	Armature	70.6	71.1
10a	Yoke bars	18.8	18.2
10b	Yoke bars	18.1	17.1
10c	Yoke bars	15.6	15.2
10d	Yoke bars	14.2	13.6
11	End of yoke bracket, commutator side	8.7	8.6
12	Yoke bracket opposite pole, commutator side	5.7	5.4
13	End of yoke bracket, pulley side	12.1	11.4
14	Yoke bracket opposite pole, pulley side	9.1	8.1
15	Middle of yoke bracket, pulley side	7.7	6.9
	The value of "v" is	1.42	1.40

THE WESTON INCANDESCENT DYNAMO.

This dynamo is of the well-known double magnetic circuit form, made to run 60 70 volt 16 candle-power lamps. The magnet spools, four in number, are placed horizontally and wound on wrought-iron elliptical cores 8 inches long with axes about 5 and 11 inches. The yoke pieces are of cast iron, practically rectangular in cross section, with an area of about 38 square inches. The two pole-pieces are also of cast iron, with a section of about 90 square inches. The total

length of a single magnetic circuit is about 45 inches. Figure 4 shows the positions of the exploring coils used. The composition bearing at the pulley end of the shaft is held by arms which project from the upper and lower pole piece, and come so near together that it would seem as if together with the shaft a very good path was available for stray lines of force. Coil 7 was wound upon one of the iron supports, and is not shown on the figure.

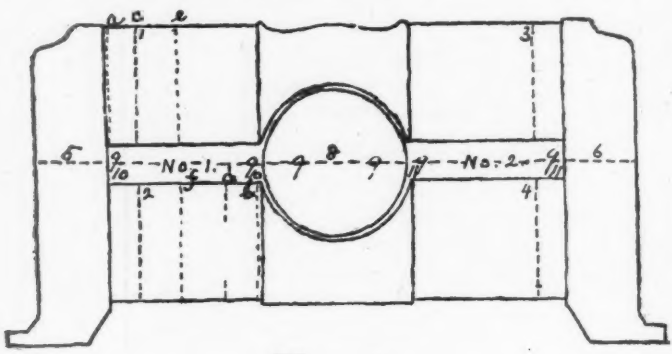


FIG. 4.

EXPLORING COILS.

Coil.	Turns.	Position.
1	1	Upper magnet spool No. 1, two inches from yoke.
2	1	Lower magnet spool No. 1, two inches from yoke.
3	1	Upper magnet spool No. 2, two inches from yoke.
4	1	Lower magnet spool No. 2, two inches from yoke.
5	1	Yoke No. 1.
6	1	Yoke No. 2.
7	10	Pulley bearing arm.
8	1	Armature.
9	1	Whole plane.
10	10	Between spools magnet No. 1.
11	10	Between spools magnet No. 2.

One half of the sum of the deflection from coils 1, 2, 3, 4, is taken as 100 per cent. in the table of percentage distribution. The four values were almost identical, indicating a very good balance of the windings.

WESTON INCANDESCENT DYNAMO.

Percentage Distribution of Magnetization.

Coil.	Position of Coil.	Mag.	Demag.
1 & 2	Upper and lower magnet spool No. 1	100.0	100.0
3 & 4	Upper and lower magnet spool No. 2	100.0	100.0
5	Yoke No. 1	93.3	93.0
6	Yoke No. 2	93.3	93.0
7	Pulley bearing arm	3.7	3.7
8	Armature	78.9	78.8
9	Whole plane	91.8	93.0
10	Between spools No. 1	3.3	3.3
11	Between spools No. 2	3.4	3.4
1a	. . . . .	98.5	98.5
1c	. . . . .	100.0	100.0
1e	. . . . .	98.5	98.5
2f	. . . . .	99.0	98.5
2d	. . . . .	95.8	95.9
2b	. . . . .	91.5	92.4
	The value of "v" is	1.27	1.27

THOMSON–HOUSTON MOTOR.

This motor has magnets of the inverted type of single magnetic circuit; the yoke is cast in one piece with the bed-plate. The armature bearings are supported by iron pillars from the bed-plate. The vertical magnet cores are of circular section about $7\frac{1}{2}$ inches in diameter and $8\frac{3}{4}$ inches long. The pole pieces are 10 inches long and $8\frac{1}{2}$ inches high. As this machine was in almost constant use, only a few

measurements could be taken, and are given only as interesting in connection with this paper, and not as the result of a careful and complete study of the waste field.

Coil 5 was arranged to see if there was a great leakage between the horns of the pole pieces, which appear to be very close together.

THOMSON–HOUSTON 220 VOLT, 10 H.P. MOTOR.

Percentage Distribution of Magnetization.

Coil.	Position of Coil.	Mag.	Demag.
1	Magnet spool 2 inches from yoke. Maximum	100.0	100.0
2	Magnet spool at yoke	99.0	99.6
3	Magnet spool at pole piece	91.4	92.2
4	Armature	75.9	75.1
5	Around armature, 1 inch from it	78.1	78.6
	The value of "v" is	1.32	1.33

THE EDDY DYNAMO.

This machine was a special one made for the Mining Department of the Massachusetts Institute of Technology for a maximum output of 50 ampères at 50 volts. The old style Eddy motor frame was used in this machine, and at the request of the Eddy Company tests were made of magnetic leakages, efficiencies, etc., both with and without certain iron and composition parts. The object was to learn what could be done to improve the design of the machine, and incidentally to find out just what difference would be made by the substitution of some non-magnetic metal for iron in the construction of the bearing supports and pulley.

The method of studying the magnetic losses was substantially the same as already described, except that the results were calculated from the mean of the deflections produced by magnetizing and demagnetizing.

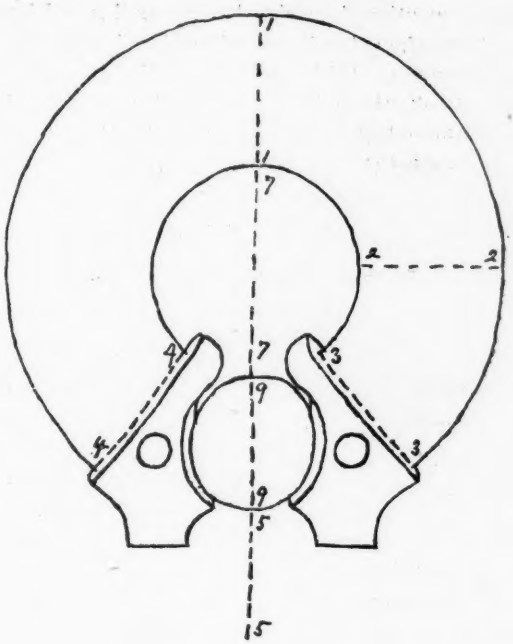


FIG. 5.

EXPLORING COILS.

Coil.	Position.
1	Top of magnet.
2	Side of magnet.
3	Side of magnet close to pole piece.
4	Side of magnet close to pole piece.
5	Space between armature and floor.
6	Space, including commutator and bearing.
7	Between magnet coils.
8	Space, including pulley and bearing.
9	Armature.

The "parts" mentioned consisted of the pulley and four large pins which screwed into the pole pieces and furnished supports for the composition bearing pieces. With the iron parts in place, there was a partial magnetic circuit through the two pulley bearing pins and the pulley, and also through the two commutator bearing pins, and the iron rocker-arm that carried the brushes.

EDDY DYNAMO.

Percentage Distribution of Magnetization.

Coil.	Position.	Composition.	Iron.
1	Top of magnet	100.0	100.0
2	Side of magnet	95.0	95.6
3	Pole piece	88.1	88.9
4	Pole piece	88.5	89.4
5	Base	8.46	7.24
6	Commutator side	2.23	5.43
7	Between magnet coils	6.23	5.68
8	Pulley side	2.60	3.98
9	Armatures	66.9	61.4
	The value of "v" is	1.49	1.63

It is quite evident that with the iron parts in place there is less leakage of lines of force from the sides of the magnet, in the space over the armature and under the machine; but that the loss at the commutator side is increased about 100%, and at the pulley side about 65%, causing a loss of 8.8% in the armature. The change from iron to composition parts increased the commercial efficiency of the machine by about 1.6%, not however, so much by a saving in the energy spent in the magnet as by reducing the eddy currents in the iron pulley which became very perceptibly hot while running. Since these tests were made, this machine has been very greatly improved.

The following table gives the values of "v" as found by W. B. Esson, together with the values given in this article:

Machine.	Field.	Armature.	Remarks.	"v."
Edison-Hopkinson	Single magnet.	Drum . .	Poles next bed-plate . . .	1.32
Siemens	Single magnet.	Drum . .	Yoke next bed-plate . . .	1.30
Phœnix	Single magnet.	Cylinder.	Yoke next bed-plate . . .	1.32
Phœnix	Double magnet	Cylinder.	Horizontal	1.40
Manchester . . .	Double magnet	Cylinder.	Bed and one pole common .	1.49
Victoria	Double magnet	Ring . .	Ordinary pattern	1.40
Ferranti	Double magnet	Coreless.	Alternating	2.00
Edison	Single magnet.	Drum . .	. . . . .	1.53–1.57
Thomson-Houston	Single magnet.	Sphere .	. . . . .	1.42–1.40
Weston	Double magnet	Drum . .	. . . . .	1.27–1.27
Thomson-Houston motor type . .	Single magnet.	Drum . .	. . . . .	1.32–1.33
Eddy	Single magnet.	Drum . .	Composition parts . . .	1.49
Eddy	Single magnet.	Drum . .	Iron parts	1.63

ROGERS LABORATORY OF PHYSICS,
August, 1891.

THE DIRECT DETERMINATION OF ALUMINUM IN IRON AND STEEL.[1]

By THOMAS M. DROWN and ALEXANDER G. McKENNA.

The unsatisfactory character of most, if not all, of the processes for the direct determination of aluminum in the presence of iron and phosphoric acid, and the sharpness with which both the iron and phosphoric acid can be determined, have led chemists to rely mainly on processes in which the aluminum is obtained by difference. But in the modern alloys of aluminum and iron, where the aluminum may be present only to the extent of a small fraction of one per cent., nothing short of the isolation of the aluminum itself can give satisfactory evidence of its presence.

In the course of some experiments on the electrolytic deposition of metals we have found that it is possible to remove iron completely from its acid solution in large quantity and in short time, by a current that will not in the least affect the aluminum in solution. The essential condition of success in this operation is the use of mercury as a cathode, the iron forming an amalgam with the mercury as fast as it is deposited from solution. This use of mercury was proposed by Dr. Wolcott Gibbs, in a paper read before the National Academy of Science in 1883, as a method of determining many metals by electrolysis which are not at all, or only imperfectly, deposited on a platinum cathode. It is certainly one of the most valuable and suggestive contributions to the quantitative separation and determination of metals by electrolysis that has yet been made.

The following are some of the experiments we have made to determine the conditions of success in the application of the method to the determination of aluminum in the presence of iron:

First, as to the completeness of the precipitation of the iron. The

[1] Abstract from Thesis, Course V, 1891, read at the Cleveland meeting, American Institute of Mining Engineers, June, 1891.

first attempts to determine the iron which had been removed from the solution and alloyed with the mercury showed an apparent loss, notwithstanding the fact that the iron was completely removed from solution. This was subsequently found to be due to the volatilization of some of the mercury on drying before weighing. The amount of mercury which may be thus lost is very considerable, as the following experiments show.

About 75 grams of mercury were put into a beaker, which was then weighed. It was washed several times with water, and once or twice with alcohol. The loss on drying different times and at different temperatures was as follows:

Time of Drying.	Temperature.	Loss, Gram.
10 minutes	140° C.	.0096
10 minutes	100°	.0043
10 minutes	100°	.0028
10 minutes	100°	.0030
10 minutes	100°	.0030
10 minutes	100°	.0025
2 hours	70°	.0040
5 hours	70°	.0120
20 hours	70°	.0520
48 hours	25°	.0030
48 hours	24°	.0025
24 hours	24°	.0007
24 hours	24°	.0012
48 hours	24°	.0042
48 hours	24°	.0033

But it is, in fact, only necessary to heat the mercury for about two minutes at a temperature of 100° C. to free it completely from moisture, and in this time the loss is very small. The following are the amounts lost in nine experiments under these conditions: .0002, .0005, .0005, .0003, .0008, .0005, .0002, 0, 0, — an average of 0.00033 gram.

There seems also, at times, to be a loss not connected with the volatilization of the mercury, which, possibly, may be due to impuri-

ties in the mercury, metals, for instance, which are dissolved out by the acid, and not precipitated on the mercury again. On this account it is desirable, in cases where the process is used to determine iron or other metal, to have a blank beaker in the circuit, containing only the mercury and dilute sulphuric acid, and to add any loss which may be found in this beaker to the amount found in the others in the series.

The following are a series of results obtained by electrolyzing a solution of ferrous ammonium sulphate, slightly acidulated with sulphuric acid.

Iron Taken. Gram.	Iron Found. Gram.	Loss of Weight in Blank. Gram.	Iron Found + Loss in Blank. Gram.
.2260	.2254	Not made.	. . .
.3727	.3725	Not made.	. . .
.3080	.3089	Not made.	. . .
.3238	.3232	Not made.	. . .
.0647	.0632	.0020	.0652
.0647	.0634	Not made.	. . .
.0647	.0649	0000	.0649
.0647	.0635	Not made.	. . .
.0604	.0602	.0003	.0605
.0604	.0608	.0003	.0611
.3020	.3008	.0003	.3011
.3020	.3000	.0003	.3003

The best conditions for the rapid precipitation of the iron are a strong current (about 2 ampères or 20 cc. of electrolytic gas a minute), a nearly neutral solution of small bulk, a large amount of mercury (not less than fifty times the weight of the iron to be precipitated), and a large anode of platinum. The mercury cathode is brought into the circuit by means of a platinum wire inclosed and fused into one end of a glass tube, which passes through the liquid. It is of advantage to pour mercury into this tube to the depth of an inch, in order to weight it and make the connection with the mercury cathode more stable.

By observing the above conditions it was found practicable to precipitate 10 grams of iron in from 10 to 15 hours. The iron amalgam may contain as high as 10 per cent. of iron. On standing a long time exposed to the air, the iron separates out as a black powder, which may be removed from the mercury by agitation with water. Mercury which has been used for iron precipitations may be purified by removing the greater part of the iron amalgam by filtration through chamois skin, and then passing air through the filtered portion, as recommended by J. M. Crafts.

Second, as to the behavior of manganese in solution under the foregoing conditions. Inasmuch as manganese is almost always present in iron and steel, a good many experiments were made to find what becomes of it under the electrolytic conditions which we have been considering. It was found that a portion is oxidized to the dioxide, coating the platinum anode, and ultimately falling off, in great part, in scales, and that a portion is reduced to the metallic state, and alloys with the mercury. This fact of the reduction of the manganese was evident on electrolyzing a solution containing only dilute sulphuric acid, using as a cathode mercury which had been previously used in an experiment with a manganese solution. In a few minutes the permanganate color appeared, and a slight coating of manganese dioxide was deposited on the anode. The experiments made to determine what proportion of manganese was reduced and what proportion oxidized were not satisfactory, but in general it may be said that about half the manganese alloys with the mercury; the other half is nearly all oxidized, and is found both on the anode and in scales floating in the liquid. A small portion is always found in solution. By using both electrodes of platinum it was found possible, in the absence of iron, to precipitate manganese completely as dioxide; but the coating on the anode was never coherent when more than mere traces of manganese were present. But the danger of the re-solution of the floating particles of the manganese dioxide, together with the necessity of filtering and igniting it to the proto-sesquioxide, makes the process an unsatisfactory one for the determination of manganese. The best conditions were found to be a concentrated solution of manganese sulphate to which a little nitric acid had been added, a rather weak current, a small cathode, and a large anode.

Third, as to the influence of phosphoric acid on the precipitation of iron. Two solutions containing equal amounts of iron were elec-

trolyzed in series. To one was added one gram of crystallized hydrogen di-sodium phosphate, and to the other dilute sulphuric acid. When the iron was all precipitated, the beakers with the mercury, together with the glass tubes containing the platinum wires, were weighed, and found to have gained, respectively, 0.1290 and 0.1275 gram. To a solution of 3 grams of iron in sulphuric acid, 0.1935 gram crystallized hydrogen di-sodium phosphate was added, equivalent to .0167 phosphorus. After the iron was completely removed from the solution, the phosphoric acid was precipitated by magnesium mixture, and .0163 gram phosphorus obtained. A duplicate experiment gave .0161 gram phosphorus. A third experiment with the same amount of iron gave, under like conditions, .0064 gram phosphorus when .0068 was added. From the experiments we may conclude that the separation, by this electrolytic method, of iron and phosphoric acid in solution is satisfactory.

Fourth, as to the separation of iron and aluminum. Known amounts of iron and aluminum in solution together as sulphates were electrolyzed, and, after all the iron had been deposited, the alumina was precipitated by ammonia. Following are two results thus obtained:

Alumina Taken. Gram.	Alumina Found. Gram.	Iron Taken. Gram.	Iron Found. Gram.
.0283	.0286	.2286	.2277
.0142	.0142	.2286	.2283

The iron, determined by weighing the mercury after electrolyzing the solution, includes in both cases a blank of .0020 gram, which was the loss of a mercury cathode in the same series, when dilute sulphuric acid only was electrolyzed.

The process was now tried under the conditions which would obtain in the determination of aluminum in iron and steel, namely, known amounts of aluminum sulphate were added to a known amount of steel. After much experimenting the following procedure was adopted as being the most uniformly satisfactory.

Dissolve 5 to 10 grams of iron or steel in sulphuric acid, evaporate until white fumes of sulphuric anhydride begin to come off, add water, heat until all the iron is in solution, filter off the silica and carbon, and wash with water acidulated with sulphuric acid. Make the filtrate nearly neutral with ammonia, and add to the beaker, in which the electrolysis is to be made, about one hundred

times as much mercury as the weight of iron or steel taken. The bulk of the solution should be from 300 to 500 cc. Connect with the battery or dynamo current in such a way that about two amperes may pass through the solution over night. This we have generally accomplished by using three lamps of 32 candle-power arranged in parallel on an Edison circuit. In the morning the solution is tested for iron, and, if necessary, the electrolysis is continued after adding enough ammonia to neutralize the acid that has been set free by the deposition of the iron. The progress of the operation may be observed by the changing color of the solution. At first it becomes darker in color near the anode; after five or six hours it is nearly colorless, and finally becomes pink, from the formation of permanganate.

When the solution gives no test for iron, it is removed from the beaker with a pipette while the current is still passing. When as much has been removed as possible without breaking the current, water is added, and the operation continued until the acid has been so far diluted that there is no danger of dissolving iron from the mercury. The anode is now taken out, and the mercury washed with water until the last traces of the solution have been removed from it. After filtering, to remove any flakes of manganese dioxide which may be suspended in the solution, sodium phosphate is added in excess, and 10 grams of sodium acetate. The solution is now made nearly neutral with ammonia, and boiled for not less than forty minutes. The precipitate of aluminum phosphate is then filtered off, ignited, and weighed. It should be white after ignition. If it has more than the faintest shade of color it must be dissolved by fusing with acid potassium sulphate, and again electrolyzed for two or three hours. The second precipitate has been found to be always white without a trace of iron; but, in general, we have found the first precipitate to be free from iron, or to contain such a minute amount that the second treatment is not necessary. We have determined that .0003 gram of iron will give a decided red color to .0076 gram of aluminum phosphate. The precipitate of aluminum phosphate, produced as above, does not always have the composition $Al_2O_3P_2O_5$. Our analyses of it go to show that the formula $7Al_2O_36P_2O_5$ more nearly expresses its average composition, and in those cases in which the amount of phosphoric acid and alumina have not been actually determined in the precipitate, we have assumed this composition, which is equivalent to 24.14 per cent. of aluminum in the precipitate.

It is necessary to boil for at least forty minutes to precipitate completely the aluminum phosphate, and excessive washing of the precipitate should be avoided.

The following table gives the result obtained in determining by the above process the aluminum added in known amounts to solutions of steel:

Steel Taken. Grams.	Per cent. of Aluminum added.	Per cent. of Aluminum found.
5	0.39	0.36
5	0.39	0.38
5	0.39	0.38
5	0.39	0.38
5	0.39	0.37
5	0.043	0.045
5	0.043	0.041
5	0.043	0.049
5	0.043	0.048
10	0.027	0.015
10	0.200	0.160
10	0.046	0.044
5	0.085	0.088

A blank experiment with the same steel, without the addition of any aluminum, gave a precipitate of aluminum phosphate equivalent to 0.004 per cent. of aluminum, which has been deducted from the results in the above determinations. This small amount came, doubtless, from the reagents and the glass vessels used, and may have been partly silica. This correction should be made in all cases where the amount of aluminum is very small.

A sample of Mitis steel analyzed by this method gave the following result:

Steel Taken. Grams.	Aluminum Found. Per Cent.
4.4260	0.014
4.4260	0.013
12.6650	0.014

A sample of "aluminum physic" used in the preparation of Mitis castings gave as follows:

Iron Taken. Grams.	Aluminum Found. Per Cent.
1.6130	6.28
0.4030	6.52
0.4030	6.22

A sample of pig-iron to which aluminum had been added in remelting gave as follows:

Iron Taken. Grams.	Aluminum. Per Cent.
1.4576	0.789
1.8167	0.806
1.6390	0.794
1.6130	0.802

It might be thought that the process would be simplified by reducing the iron to the state of protoxide, and then precipitating the alumina as basic acetate, subsequently removing by electrolysis the small amount of iron precipitated with the alumina. A number of experiments proved, however, that this modification not only gave less accurate results, but involved much more work than the precipitation of all the iron by electrolysis. When the iron is all removed over night without involving any work on the part of the analyst, it is surely superfluous to go through a more or less tedious chemical operation to remove a part of the iron.

It is obvious that this process of electrolysis with a mercury cathode may be of value in other analytical operations in which the removal of the iron would be of advantage; as, for instance, in the determination of phosphoric acid by magnesia.

CONTRIBUTION TO OUR KNOWLEDGE OF ORTHODICHLORSTILBENE.[1]

By AUGUSTUS H. GILL, PH.D.

INTRODUCTION: Onufrowicz[2] obtained by the action of finely-divided copper upon benzalchloride, stilbene chloride, according to the equation: —

$$2C_6H_5\,CHCl_2 + 2Cu = C_6H_5\,CHCl - CHCl\,C_6H_5 + 2CuCl.$$

If, however, the compound in which one of the hydrogen atoms in the ring had been substituted by chlorine — orthochlorbenzalchloride — was employed, similar results were to be expected, and orthodichlorstilbene chloride would be formed: —

$$2C_6H_4 < \overset{Cl}{CHCl_2} + 2Cu = C_6H_4 < \overset{Cl}{CHCl} - \overset{Cl}{ClHC} > C_6H_4 + 2CuCl.$$

If this compound be treated with an insufficient quantity of alcoholic potash, as stilbene dichloride was treated by Laurent,[3] it is to be expected that only one molecule of hydrochloric acid would be split off, and orthodichlortolane hydrochloride result: —

$$C_6H_4 < \overset{Cl}{CHCl} - \overset{Cl}{ClCH} > C_6H_4 + KOH = C_6H_4 < \overset{Cl}{CH} = \overset{Cl}{ClC} > C_6H_4 + KCl + H_2O.$$

If a large excess of alcoholic potash be present, then the reaction would take place, according to Fittig,[4] with the formation of orthodichlortolane: —

$$C_6H_4 < \overset{Cl}{CHCl} - \overset{Cl}{ClCH} > C_6H_4 + 2KOH = C_6H_4 < \overset{Cl}{C} \equiv \overset{Cl}{C} > C_6H_4 + 2KCl + 2H_2O.$$

[1] Inaugural Dissertation presented to the Philosophical Faculty of the University of Leipsic for the degree of Doctor of Philosophy, July, 1890.

[2] Berichte der deutschen chemischen Gesellschaft, 17, 835.

[3] Berzelius' Jahresbericht, 25, 616. [4] Liebig's Annalen, 168, 74.

If zinc dust be substituted for potash, it should remove two atoms of chlorine, and dichlorstilbene should be formed: —

$$C_6H_4 < \begin{matrix} Cl \\ CHCl \end{matrix} - \begin{matrix} Cl \\ ClHC \end{matrix} > C_6H_4 + Zn = C_6H_4 < \begin{matrix} Cl \\ CH = \end{matrix} \begin{matrix} Cl \\ HC \end{matrix} > C_6H_4 + ZnCl_2.$$

Were it then possible to remove the other chlorine atoms from this compound by the use of sodium or potassium, a new synthesis of phenanthrene would be accomplished: —

$$C_6H_4 < \begin{matrix} Cl \\ CH = \end{matrix} \begin{matrix} Cl \\ HC \end{matrix} > C_6H_4 + 2Na = \overline{C_6H_4 - CH = CH - C_6H_4} + 2NaCl.$$

This line of thought was suggested to me as a subject for a thesis by Professor Johannes Wislicenus, of the University of Leipsic. The following pages contain the results of the investigation.

PREPARATION OF ORTHOCHLORBENZALCHLORIDE.

According to Henry[1] this compound is readily obtained by the action of phosphorus pentachloride upon salicyl aldehyde; but the resulting oxychloride and excess of pentachloride are not easily separated from the product. To avoid this difficulty, orthochlortoluol was prepared, and this chlorinated at its boiling point. Its preparation took place as follows: 100 grams orthotoluidine were gradually poured into a mixture of 200 cc. hydrochloric acid (sp. gr. 1.16) and 300 cc. water, the resulting chloride not being wholly dissolved. To this was gradually added a solution of 90 grams 86% sodium nitrite in 150 cc. of water, the temperature being kept below 10°. Usually during the addition of the last portion of the nitrite solution there was a slight evolution of nitrogen, hence it is advisable to have an excess of hydrochloric acid present; the diazo body resulting remained dissolved. The mixture was allowed to stand half an hour to complete the reaction and then gradually poured into 1800 cc. of cooled hydrochloric acid (sp. gr. 1.16). The hydrochloric acid must be completely saturated. The stronger it is the better the yields obtained. An experiment with commercial acid gave only 30% of the toluidine used, when 50% was to be expected. The whole mixture was allowed to

[1] Berichte der deutschen chemischen Gesellschaft, 2, 135.

stand 18 – 24 hours, at first in a freezing mixture, and finally at ordinary temperature; it was then boiled, distilled with steam, and the oil which came over collected, washed with potassium hydrate to free it from the concomitant cresol, dried and fractionated. The portion boiling between 156° and 160° was used for chlorination; from 200 grams orthotoluidine 107 grams orthochlortoluol were usually obtained.

A steady stream of dry chlorine was passed into 100 grams orthochlortoluol heated to boiling until 50 – 55 grams were absorbed. Upon fractionation, a small quantity went over at 218°, the main portion which was used for further treatment between 226° and 230°. Upon repeated refractionation of this product, a colorless oily liquid was obtained, boiling at 228.5°, and possessing a specific gravity of 1.399 at 15°; 0.2144 gram of this compound gave 0.4724 gram AgCl, corresponding to 54.48% Cl;[1] the theory for $C_6H_4ClCHCl_2$ requires 54.77% Cl.

PREPARATION OF ORTHOCHLORBENZOTRICHLORIDE.

This body, which was first obtained by Kolbe and Lautermann[2] by the action of phosphorus pentachloride upon salicylic acid, could, as might be foreseen, be made by the further chlorination of orthochlorbenzalchloride. The high boiling residues left from the fractionation of the latter were treated with dry chlorine until saturated. The product distills between 257° and 259°, and forms under favorable conditions splendid monoclinic prisms, melting at 29°, which upon analysis yielded the following: 0.1545 gram substance gave 0.3869 gram AgCl, equivalent to 61.90% Cl. Theory for $C_6H_4ClCCl_3$, 61.70% Cl.

TREATMENT OF ORTHOCHLORBENZALCHLORIDE WITH METALS.

(1) *Copper.* Finely divided copper (*cuprum reductum*) in open vessels has no perceptible action upon the chloride; the amounts of each, the solvent, or the temperature, exercise no influence upon the result. Petroleum ethers (bpts. 55° and 120°), methyl and ethyl alcohol, benzol and toluol — liquids boiling at temperatures from 55° to 120° — were employed. A very small quantity of crystals of melting

[1] All chlorine determinations, unless it is stated to the contrary, were made according to the method of Carius.

[2] Liebig's Annalen, 115, 195.

point 97°, and also tar, were obtained, but the action is very slight; if, however, a great excess of copper is employed in sealed tubes, the yield of crystals is much increased.

(2) *Silver.* Molecular silver in alcoholic or naphtha solution (bpt. 110°) acts upon it with the formation of orthodichlorstilbene-dichloride, by the elimination of two atoms of chlorine; orthodichlorstilbene was also obtained in small quantities. Silver has a much more energetic action than copper in sealed tubes at 120° – 130°, with the formation of much tar and fewer crystals of orthodichlorstilbene.

(3) *Zinc.* Upon heating the chloride in naphtha solution (bpt. 110°) with carefully purified zinc dust for eight hours, very few crystals of orthodichlorstilbene resulted; a small quantity of tar was also formed.

(4) *Sodium.* No sodium chloride was formed upon heating the chloride with sodium wire in sealed tubes at 160° for eight hours.

It may be due to the fact that this is a disubstituted compound that the metals have so little action upon it; these bodies are apparently the most stable, as shown by the following facts. Let us consider the chloracetic acids: —

(a) *Monochloracetic acid.* It is slowly decomposed by water. Buchanan.[1]

(b) *Dichloracetic acid.* It is much more slowly decomposed by water. Beckurts and Otto[2]. If both acids be boiled with water, then in

4 hours	11%	CH_2Cl	COOH	is decomposed,	and in	5 hours	but	1.3%	$CHCl_2$	COOH
11	"	23%	"	"	"	"	10	"	"	1.83%	"
37	"	56%	"	"	"	"	40	"	"	7.06%	"
96	"	82%	"	"	"	"	100	"	"	12.4%	"

(c) *Trichloracetic acid.* The aqueous solution rapidly decomposes upon boiling into carbonic acid and chloroform. Beckurts and Otto.[3] It is evident then that the dichloracetic acid is the most stable.

The chlorine derivatives of toluol exhibit a similar characteristic.

[1] Berichte der deutschen chemischen Gesellschaft, 4, 341.
[2] Berichte der deutschen chemischen Gesellschaft, 14, 583.
[3] Berichte der deutschen chemischen Gesellschaft, 14, 589.

(a) *Benzylchloride.* Limpricht[1] says, "Sodium decomposes benzylchloride when heated." "When it is boiled with water for twenty-three hours, it is almost completely decomposed." Niederist.[2] Zincke[3] states that finely divided copper acts vigorously upon benzylchloride when heated, forming cuprous chloride and evolving hydrochloric acid.

(b) *Benzalchloride.* "Sodium and potassium can be boiled together with 'chlorobenzol' (heated to 206°) without the metal losing its luster or the slightest trace of the chloride being formed." Wicke.[4]

"When 'chlorobenzol' is boiled together with sodium for a long time, it is decomposed with the formation of a brown resin." Beilstein.[5]

"Boiling 'chlorobenzol' is in reality, although very slowly, somewhat decomposed by sodium." Limpricht.[6]

Cahours[7] could obtain no trace of benzaldehyde upon heating "benzolchloride" with water in sealed tubes at 130°–140°. Limpricht[8] obtained benzaldehyde in "varying quantities" under the same conditions, except a higher temperature, 160°, was employed. Lippmann and Hawliczek[9] were unable to obtain it until a temperature of 250° was attained. Onufrowicz[10] obtained stilbene chloride by treatment with copper at 100.°

(c) *Benzotrichloride.* Limpricht[11] obtained benzoic acid from this compound by the action of water in sealed tubes at 140°–190°. Hanhart[12] remarks, "Benzotrichloride is energetically acted upon by copper when gently warmed." When boiled upon the water bath with sodium for eight hours, a perceptible quantity of sodium chloride is formed. Here, as in the previous case, the disubstituted body is least acted upon.

[1] Liebig's Annalen, **139**, 306.
[2] Liebig's Annalen, **196**, 353.
[3] Berichte der deutschen chemischen Gesellschaft, **2**, 739; **4**, 298.
[4] Liebig's Annalen, **102**, 363.
[5] Liebig's Annalen, **116**, 349.
[6] Liebig's Annalen, **139**, 317.
[7] Liebig's Annalen, Supplementband **2**, 306.
[8] Liebig's Annalen, **139**, 319.
[9] Berichte der deutschen chemischen Gesellschaft, **9**, 1462.
[10] Berichte der deutschen chemischen Gesellschaft, **17**, 835.
[11] Liebig's Annalen, **139**, 324.
[12] Berichte der deutschen chemischen Gesellschaft, **12**, 681.

PREPARATION OF ORTHODICHLORSTILBENE CHLORIDE.

Fifteen grams of orthochlorbenzalchloride were dissolved in 70 grams methyl alcohol, and heated upon an oil bath for six hours to 95°, with a mixture of 25 grams (3 mols.) molecular silver and 25 grams ignited sea sand. The hot alcoholic solution was separated from the silver and the alcohol evaporated in a current of dry air until a sirup began to separate out. The crystals which were obtained at the same time were pressed between filter paper and crystallized after the following method: petroleum ether boiling from 33° to 55° was added to the ethereal solution, until a cloud was formed; it was then filtered and evaporated in a current of dry air. By this means the body was obtained as white rhombic crystals of melting point 170.5°, and analyzed as follows:

I. 0.2415 gram yielded 0.0682 gram H_2O and 0.4613 gram CO_2, 0.2378 gram gave 0.4239 gram AgCl.

II. 0.1859 gram yielded 0.0537 gram H_2O and 0.3546 gram CO_2, 0.2149 gram gave 0.3841 gram AgCl.

Calculated for $C_{14}H_{10}Cl_4$.		Found.	
		I.	II.
C 52.50		52.10	52.01
H 3.12		3.06	3.21
Cl 44.37		44.06	44.20

The compound is easily soluble in ether and chloroform, difficultly in methyl alcohol and absolute ethyl alcohol and naphtha. The yield is about 5% – 8% of the orthochlorbenzalchloride employed.

PREPARATION OF ORTHODICHLORSTILBENE.

Twenty-five grams orthochlorbenzalchloride are poured upon a mixture of 33 grams (4 mols.) of reduced copper and 66 grams ignited sea sand, which is contained in the tube in which the reaction is to take place. The object of the sand is to absorb the chloride completely, and to separate the particles of copper so that they do not pack together, and thus diminish the surface. The tube is now sealed and heated for 4 – 5 hours in an oil bath to 105°. Upon opening the

tube there is usually no pressure and no hydrochloric acid escapes; the tube is cut into small pieces and its contents extracted with dry acetone. The acetone solution is dried with ignited sulphate of sodium, evaporated in distilling flasks of about 50 cc. capacity and distilled at a pressure of 100 mm.

If the whole be distilled at one time, much is lost in the tar which is always formed. The main portion goes over between 160° and 260°; of this, the larger quantity boils at about 220° and crystallizes upon cooling; very little boils lower, but a considerable quantity of a resinous body still containing chlorine remains in the flask. The crystals, as obtained from absolute alcohol, are long white needles, and melt at 97°; from toluol they are rhombic crystals. The figures obtained by analysis agree with the formula $C_{14}H_{10}Cl_2$.

I. 0.1975 gram yielded 0.0741 gram H_2O and 0.4853 gram CO_2,
0.1387 gram gave 0.1601 gram AgCl.

II. 0.2371 gram yielded 0.0876 gram H_2O and 0.5813 gram CO_2,
0.2578 gram gave 0.2961 gram AgCl.

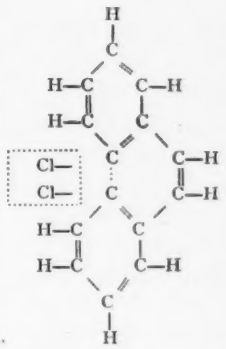
Calculated for $C_{14}H_{10}Cl_2$.		Found.	
C	67.47	I. 67.14	II. 66.90
H	4.01	4.17	4.00
Cl	28.51	28.53	28.38

Orthodichlorstilbene is readily soluble in alcohol, ether, benzol, toluol, chloroform and carbon bisulphide, difficultly in naphtha (bpt. 110°); the yield is 10% – 12% of the chloride used.

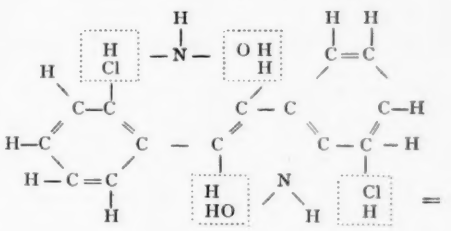
The compound can have either the formula

$$C_6H_4Cl-C-H \quad \text{or} \quad C_6H_4Cl-C-H$$
$$\quad\quad\quad

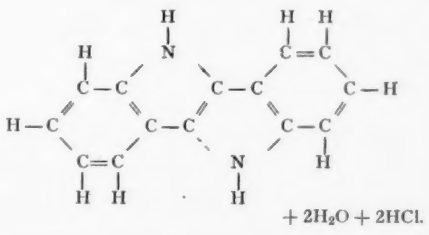
To this end it was treated in alcoholic solution with zinc dust, and also in a sealed tube at 190° with metallic sodium, neither of which had the slightest action upon it. By the action of cement copper in a combustion tube at a red heat, a small quantity of chloride of copper was formed, and also a small quantity of an oil that still contained chlorine. Similar results were obtained under like conditions with zinc dust.



If, however, the compound possessed the axial-symmetric formula, then when heated with hydroxylamine it should give a double pyrrol derivative, $C_{14}H_{10}N_2$.



Upon heating in a sealed tube with hydroxylamine for five or six hours, to 140°, no reaction was perceptible. Aniline and alcoholic ammonia under the same conditions were without action.



$+ 2H_2O + 2HCl.$

All attempts to change the compound into an isomer by the usual method of heating to 190° were fruitless. If the body in boiling chloroform solution be treated with chlorine, there results after cooling, a white crystalline compound which is identical with the orthodichlorstilbene dichloride previously described. It melts at 170.5°, and upon analysis, 0.2468 gram substance gave 0.4449 gram AgCl or 44.47%; the theory requiring 44.37% chlorine.

PREPARATION OF ORTHOCHLORTOLANE HYDROCHLORIDE.

The dichloride, when treated with one molecule of sodium hydrate in alcoholic solution in a sealed tube at 100°, gave a white substance

crystallizing in scales of a melting point of 66° and easily soluble in alcohol and ether. It corresponds with the formula $C_{14}H_9Cl_3$ as the analysis shows.

I. 0.2370 gram substance gave 0.3560 gram AgCl.
II. 0.2103 " " " 0.3212 " " (according to lime method).

Calculated for $C_{14}H_9Cl_3$.	Found.	
Cl 37.49	I. 37.14	II. 37.76

The reaction by which the body was formed is as follows: —

$$C_6H_4<\begin{matrix}Cl\\CHCl-ClCH\end{matrix}>\begin{matrix}Cl\\\end{matrix}C_6H_4+NaOH=C_6H_4<\begin{matrix}Cl\\CH=ClC\end{matrix}>\begin{matrix}Cl\\\end{matrix}C_6H_4+NaCl+H_2O.$$

PREPARATION OF ORTHODICHLORTOLANE.

If in the preceding reaction an excess of sodium hydrate be used, then two molecules of hydrochloric acid are split off according to the equation

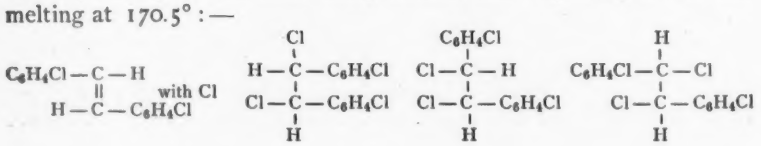
$$C_6H_4<\begin{matrix}Cl\\CHCl-ClHC\end{matrix}>\begin{matrix}Cl\\\end{matrix}C_6H_4+2NaOH=C_6H_4<\begin{matrix}Cl\\C=C\equiv\end{matrix}\begin{matrix}Cl\\C\end{matrix}>C_6H_4$$
$$+NaCl+2H_2O,$$

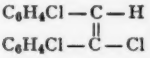
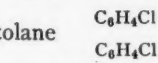
and white rhombic tables of melting point 88°–89° are the result. These are the orthodichlortolane, and are easily soluble in alcohol and ether. The analysis: —

I. 0.2824 gram yielded 0.0905 gram H_2O and 0.7019 gram CO_2.
I. 0.2246 " " 0.2604 " AgCl.
II. 0.2242 " " 0.2571 " "

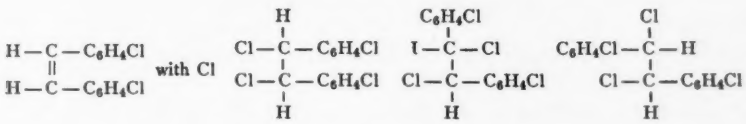
Calculated for $C_{14}H_8Cl_2$.	Found.	
	I.	II.
C 68.01	67.79	
H 3.24	3.56	
Cl 28.75	28.67	28.43

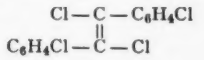
By the treatment of the axial-symmetric body with chlorine, it is possible to form the three following compounds, of which the first would probably be the most easily formed, and very likely is the one melting at 170.5°: —

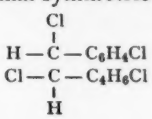


If this compound be treated with one molecule of potassium hydrate, there would be formed from all three the plane symmetric orthodichlortolane hydrochloride  , with an excess of potassium hydrate, orthodichlortolane  . This compound would be formed the most readily from the first orthodichlorstilbene dichloride.

From the plane-symmetric orthodichlorstilbene there could be also three orthodichlorstilbene dichlorides of the following constitution: —



If these be treated with one molecule of potassium hydrate, there would be obtained from all three the axial-symmetric orthodichlortolane hydrochloride  from which the orthodichlortolane would be obtained with much greater difficulty than from the plane-symmetric.

As but one of the six possible isomers could be obtained by the addition of chlorine to orthodichlorstilbene, it is impossible to draw any very definite conclusions. From the ease with which hydrochloric acid is split off by potassium hydrate, one might conclude that the one obtained came from the axial-symmetric orthodichlorstilbene, and has probably the formula 

TRIPLE-EXPANSION EXPERIMENTAL ENGINE

In the Engineering Laboratories of the Massachusetts Institute of Technology.

By CECIL H. PEABODY, S.B.

One of the most important pieces of apparatus found in the engineering laboratories in the building recently erected on Trinity Place is the triple-expansion experimental engine, built by the E. P. Allis Company, of Milwaukee, Wisconsin. The engine is of the Corliss type, and has three cranks arranged as shown by Figures 1 and 2. The diameter of the high-pressure cylinder is 9 inches; of the intermediate cylinder, 16 inches; and of the low-pressure cylinder, 24 inches; the stroke of each is 30 inches. Each cylinder is steam-jacketed on the heads and barrel, and steam may be applied directly to any or all of the cylinders; so that by proper combinations of piping and valves the engine may be run simple, compound, or triple. The intermediate receivers are also provided with steam jackets, so that they may act as reheaters. The exhaust steam is received and condensed by a surface condenser of the marine type, which drains into an independent direct-acting air pump. The condensed water from the air pump is collected and weighed in tanks on scales, covered to avoid surface evaporation. The several jackets on the cylinders and intermediate receivers, five in all, are drained into separate receivers made of 5-ft. sections of 8-in. pipe, closed at the ends and provided with glass water-tubes and scales, so that the condensed water may be collected and measured. Provision is made for applying the indicators, gauges, and thermometers required for making a complete thermodynamic test of the engine. The cylinders, receivers, and piping are thoroughly wrapped with asbestos paper, hair felt, and lagging, or canvas.

The engine is belted to the main line of shafting running through the middle of the laboratory, and provides power for lighting the

Fig. 1.

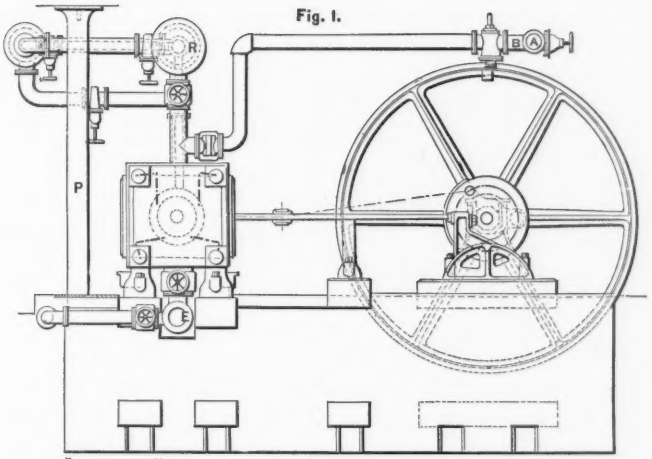
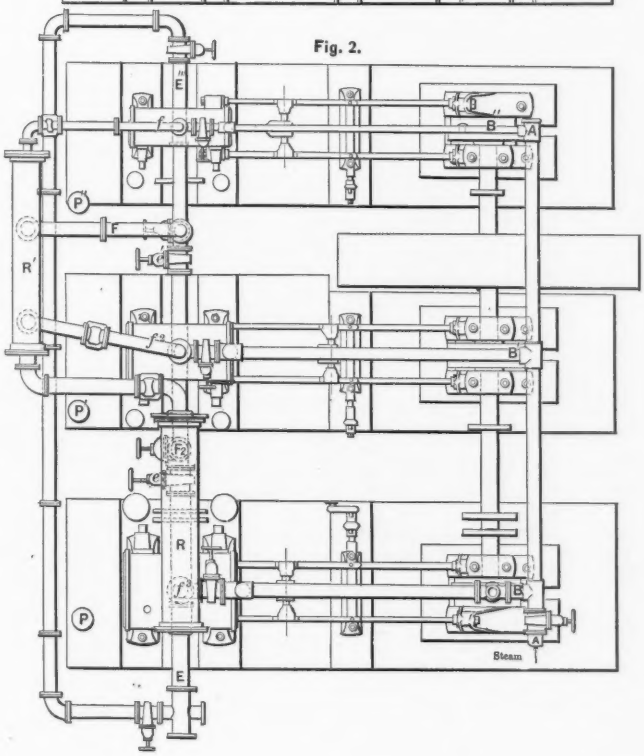


Fig. 2.



entire building by electricity, and for various tests requiring power. There are now in the laboratory, the dynamo, which absorbs about 50 horse-power; two water-cooled friction brakes that can absorb 50 horse-power each; rotary and centrifugal pumps, and other apparatus requiring power. The short section of shafting which receives the driving-belt can be uncoupled from the line-shafting running each way; considering the friction of this short section with the friction of the engine, the friction of the several lines of shafting and of the brakes when unloaded, and also the load on the dynamo, can be determined by the aid of dynamometers, and thus the load on the engine may be determined, and also the friction of the engine.

Figures 1 and 2 give an elevation and plan intended to show the general arrangement of the foundations, frames, and the piping. Parts receive the same letters in both figures. The section of the city on which the building is located being made land, the foundation was made by piling over the entire area on which the engine stands, and capping the piles with several courses of large granite blocks. From the granite the engine beds are carried up through a sub-basement so as to place the engine conveniently with reference to the engine room or basement floor. Each cylinder stands on blocks of cut stone, and is bolted through stones built into the foundation. The engine shaft is carried by splayed cast-iron bearings which are supported and bolted to the foundation in a similar manner. Each cylinder is connected to the shaft-bearings in front of it by wrought-iron rods, to take up the thrust and pull of the piston and connecting-rod. These rods are supported at about mid-length, and, from the support to the cylinder, are square, and act as guides to the crosshead. The fly wheel is placed between the high and intermediate engines, the location being decided by the fact that it is the common custom to disconnect the low-pressure cylinder, and run the high-pressure and intermediate cylinders compound and non-condensing. The cranks for the high and low pressure engines are overhung; the intermediate crank is a solid cast-steel crank bolted to flanges on the ends of the two sections of the shaft.

A 6-in. pipe A runs through the laboratory and supplies steam at about 150 lbs. pressure for heating, for various experiments, and for running the engine. At B, B′, and B″ are branches running to the several cylinders, each with a stop valve near the cylinder for the convenience of the engineer. Near B is a reducing valve or regulator,

for reducing the pressure of steam to 40 lbs. to the square inch or less, when the low-pressure cylinder receives steam direct. R and R′ are the first and second intermediate receivers. R′ is set over beyond the columns P′, P″, to make room for the driving-belt. An exhaust pipe E runs under all the cylinders, and into this each cylinder may be directly exhausted. Stop valves *e* and *e′* divide the exhaust pipe into sections when required. A valve under the low-pressure cylinder shuts it off from the exhaust pipe when the large engine is disconnected.

The high-pressure cylinder may communicate with the intermediate receiver R′ by the pipe *f* for admission, and by the pipe F for exhaust. The intermediate cylinder communicates with the receiver R′ by the pipe f_2 for admission, and with the receiver R by the pipe F_2 for exhaust. The large cylinder receives steam from the receiver R through the pipe f_3. Finally the two receivers are connected by a pipe with a stop valve as shown. There is a roundabout exhaust with valves at each end for the high-pressure cylinder. Normally the high-pressure cylinder receives steam from the pipe B″ and exhausts by the pipe F to the receiver R′; the intermediate cylinder receives steam from the receiver R′ by the pipe f_2 and exhausts to the receiver R by the pipe F_2, and the low-pressure cylinder receives steam from the receiver R by the pipe f_3 and exhausts through the valve beneath it into the pipe E.

Among the combinations rendered possible, the following may be noticed. Steam may be supplied through the reducing valve at B to the low-pressure cylinder and through the receiver R to the receiver R′, and so to the intermediate cylinder; meanwhile the high-pressure cylinder receives full-pressure steam as usual, and exhausts by the roundabout pipe; all the exhaust steam may be used for heating at about 4 lbs. back pressure. When a test is to be made, the engine is readily changed to triple-expansion condensing.

The condenser used for experimental work only, is set in a sub-basement, so that the exhaust pipe drains into it, and it in turn drains into a direct-acting air pump, from which the condensed water is received in weighing-tanks.

Steam for jacketing the high-pressure cylinder and the first intermediate receiver R′ is taken from the direct supply of steam to the high-pressure cylinder by a ¾-in. pipe; this pipe has two branches, one to the receiver and the other to the cylinder. The ¾-in. branch pipe leading to the cylinder is again branched into three parts, one to

the barrel and one to each of the heads; each of the three jackets has a pet-cock to discharge the air when the jackets are supplied with steam, and to reveal leakage of steam when the valves are shut. Thus the barrel or the heads, or both, may be jacketed with steam.

The intermediate cylinder and second receiver R are supplied with jacket steam through a ¾-in. pipe from the steam pipe B′ leading to the intermediate cylinder; a reducing valve allows the pressure on the jackets to be made lower than boiler pressure when desired. The low-pressure cylinder receives jacket steam from the pipe B before the reducing-valve, and the pipe for this purpose has its own reducing-valve to control the pressure in the jackets. The jackets are designed to carry full boiler pressure on all the cylinders when desired.

The drainage from the three jackets (*i.e.*, the barrels and two heads) of each of the cylinders is collected and led directly under the pressure in the jackets to three measuring-vessels in the sub-basement. The drainage from the receiver jackets is similarly disposed of. When the receiver jackets are not in use the receivers themselves are drained into the measuring-vessels, and an arrangement of two valves with pet-cock between makes it sure that the drainage comes from the jackets or from the receivers, as the case may be, and reveals leakage should it occur.

With the large number of large valves it is apparent that some method of detecting leakage must be devised if the tests on the engine are to receive credence. The valves are of a good type, are new, and have been carefully handled to avoid injury. Some of them may be tested for leakage while the engine is running, others can be shut and tested for leakage before the engine is started. To arrange for starting the engine a one-inch by-pass is carried round the stop valves of the intermediate and low-pressure cylinders. The by-pass pipe has two valves, and on the space between is a pet-cock that can be used to test for leakage of the valve on the by-pass pipe, or for leakage past the stop valve into the steam chest.

The three cylinders of the engine have valve gears of the Corliss type; those of the high and intermediate cylinders are arranged as usual and are moved by an eccentric acting on a wrist-plate. Vacuum dashpots insure a rapid and quiet closing of the admission valves. Since the low-pressure cylinder has a volume somewhat more than twice that of the intermediate cylinder, a special valve gear with two eccentrics is arranged as shown by Figures 3 and 4. The wrist-plate P

is moved by an eccentric with a little angular advance, suitable for giving release and compression, and is connected to the exhaust valves at V and V_1 in the usual manner. The wrist-plate P_1, outside of P, receives motion from an eccentric with a large negative, angular advance, and the admission valves are given a large lead when in mid-position in compensation. Thus the release mechanism may be arranged to give a cut-off longer than half-stroke, as the proportions of the cylinder require.

The governor is attached to the frame of the intermediate cylinder, and, by the aid of a horizontal shaft running in front of the three cylinders, may control the releasing mechanism of each of the cylinders. In Figure 4, *a* is the horizontal shaft controlled by the governor. A vertical link acts on the arm *b* of a bell-crank lever above the cylinder, and from another arm *c* a link is carried to the collar *d* on the crank and valve spindle and from thence to a collar *e* on the head and valve spindle. When desired, the governor may be disconnected by dropping the link from *a* to *b*, and the disengagement gear may then be set by hand, while the engine is running, by aid of the handwheel and screw at A; of course the hand adjustment is thrown out of gear when the governor has control of the releasing-gear. At S is a starting-bar for moving the admission valves by hand, when the gab-rod is disconnected for the admission wrist-plate.

Fig. 5.

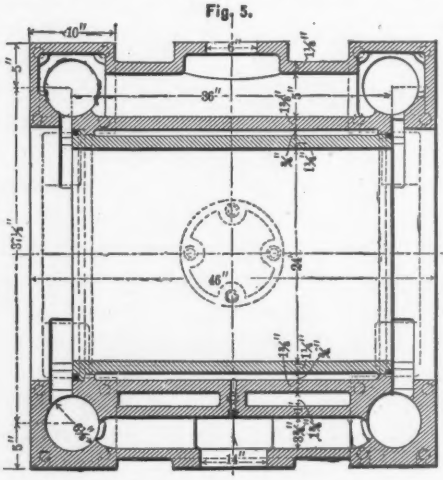
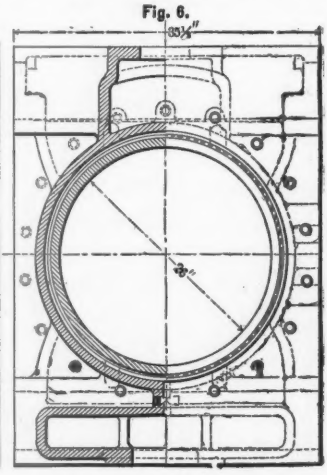


Fig. 6.



Figures 5 and 6 give transverse and longitudinal sections of the large or low-pressure cylinder. The barrel jacket is made by bush-

Fig. 3.

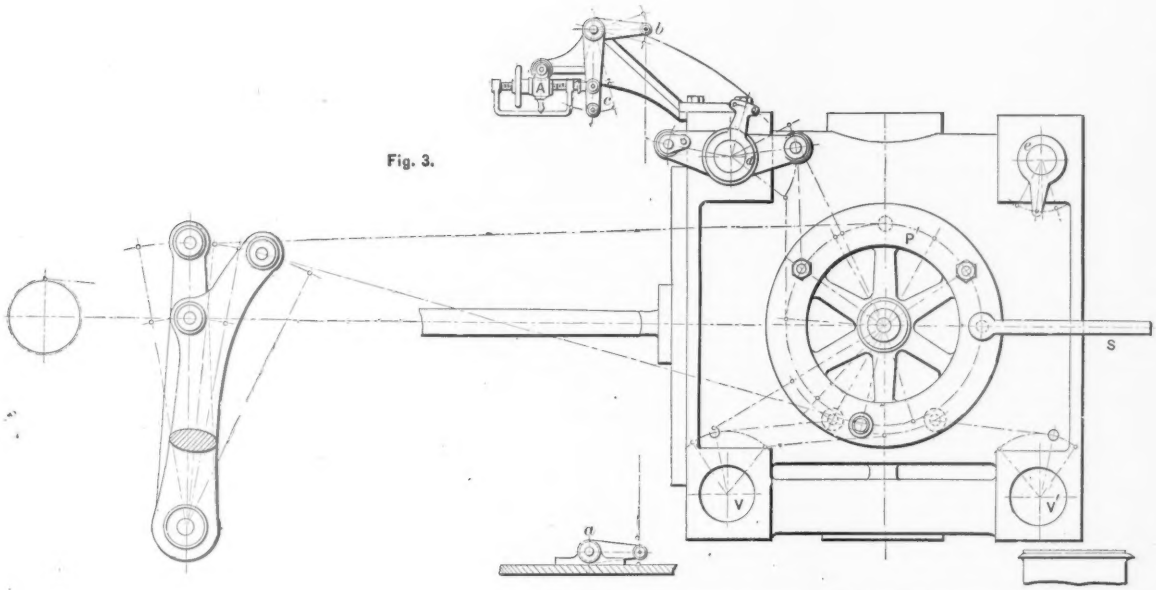
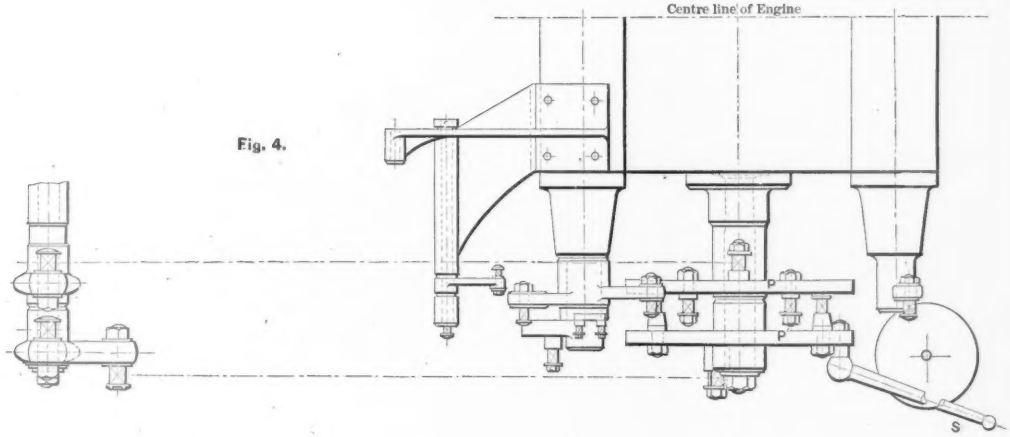
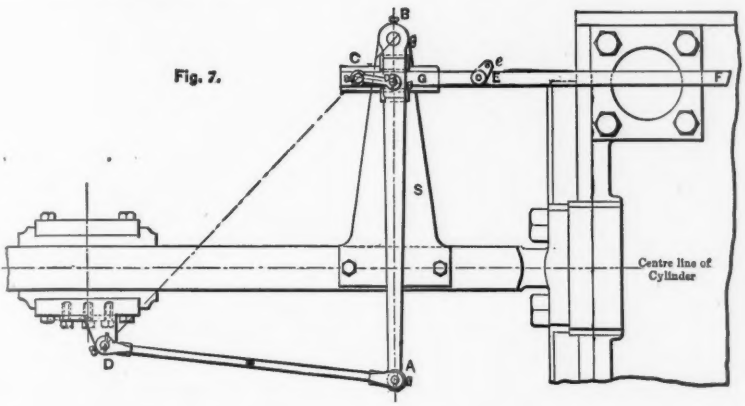


Fig. 4.



ing the cylinder-casting, as shown, the bushing being forced in under hydraulic pressure, and made tight by a ring of copper driven into a dovetail groove. The ends of the cylinders are jacketed by coring out the cylinder heads.

Fig. 7.



The indicator motion for the intermediate cylinder is shown by Figure 7. S is a standard bolted to the engine frame near the crank end cylinder head. A B is a swinging lever, connected by the link A D to the engine crosshead, and by the parallel link C G to the rod E F. The rod E F slides in guides, one on the standard S as shown, and the other on the head end valve bonnet at the right hand, and it is at the proper height for the indicator cord. The crank end indicator cord is hooked directly on to the pin *e*, which is on an arm E *e*, that can be swung up or down to give a small vertical adjustment, and clamped by a thumbscrew. The other indicator has a similar arrangement. All the joints of the indicator motion have split brass bushings and set screws to take up lost motion. When worn out the bushings can be renewed. Thus at A the link is forked, and embraces the end of the lever A B; the pin is fast in the fork, and turns in a brass bushing in the end of the lever, with a set screw near A.

Fig. 8.

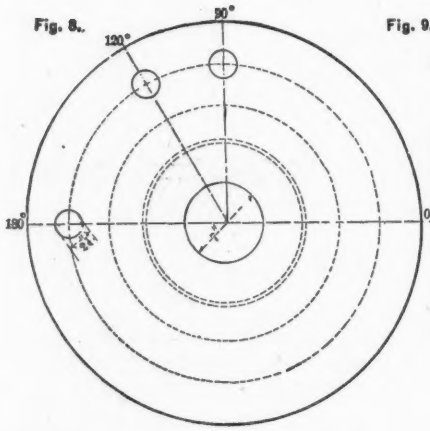
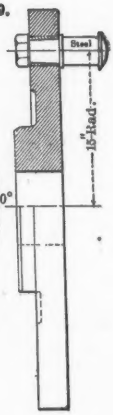


Fig. 9.



The angles at which the several cranks follow can be arranged by a device shown by Figures 8 and 9. The disc has three distinct holes bored in it, making angles of 90°, 120°, and 180°. The steel crank-pin is made tapering, and fits into a tapering steel bushing that is cut in two at one side, and part way through at seven other places. A heavy hexagonal nut on the back of the disc draws the crank-pin in till its collar bears on the face of the disc, and at the same time forces the taper bushing in, and secures the pin in the disc. This device has been found to work well on this engine, which develops about 150 horse-power, or 50 horse-power on each crank when running triple with 150 lbs. steam pressure and at 80 revolutions per minute.

APPLICATION OF HIRN'S ANALYSIS TO MULTIPLE-EXPANSION ENGINES.[1]

By CECIL H. PEABODY, S.B.

The application to simple engines of Hirn's theory, or, more properly, of Hirn's analysis of the interchange of heat between the steam and the walls of the cylinder, is now familiar to the engineering profession, through the labors of Hirn, Hallauer, Dwelshauvers-Dery, Mair, and others. But the writer has not been able to find a clear and correct statement of the analysis for compound and multiple-expansion engines. Applications of the analysis to compound engines are given by Hallauer in the form of numerical calculations only, and he contents himself with finding the heat rejected from the walls of the cylinder during exhaust. Among the very important tests on large engines reported by Mair[2] are several on compound engines; but he has united in one term the algebraic sum of the quantity of heat absorbed by the low-pressure cylinder walls during admission, and that yielded during expansion a quantity which in his tests is sometimes positive and sometimes negative, and which does not appear to have any physical meaning.

The statement of the analysis given here is a development of those given by Dwelshauvers-Dery[3] and Mair, making use of the latter's method of representing the heat equivalent of the intrinsic energy of all the fluid in the cylinder by one character. An application is given to experiments made on the triple-expansion engine in the engineering laboratories of the Massachusetts Institute of Technology.

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[1] Presented at the Providence Meeting (1891) of the American Society of Mechanical Engineers.

[2] Minutes of Proceedings of the Institution of Civil Engineers, **70**, 313; **79**, 323.

[3] Revue Universelle des Mines, **8**, 362, 1880; also Trans. Am. Soc. Mech. Engs. **11**, 72.

SIMPLE ENGINES.

Suppose that M pounds of steam are admitted to the cylinder of a simple engine per stroke, having in the supply pipe the pressure p pounds per square inch absolute, and the quality x; *i.e.*, each pound is x part steam mingled with $1 - x$ part water. The heat brought into the cylinder per stroke, reckoned from freezing point, is

$$Q = M(q + xr) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which q is the heat of the liquid and r is the latent heat of vaporization. Should the steam be superheated in the supply pipe to the temperature t_s, then

$$Q = M\,[q + r + c_p\,(t_s - t)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

in which t is the temperature of saturated steam at the pressure p, and $c_p = 0.4805$ is the specific heat of superheated steam at constant pressure.

Let the heat equivalent of the intrinsic energy of all the water and steam in the cylinder at any instant be represented by I. Let M_0 be the weight of steam caught in the cylinder at compression. Then we shall have:

at admission	$I_0 = M_0\,(q_0 + x_0\,\rho_0)$	(3)
at cut-off	$I_1 = (M + M_0)\,(q_1 + x_1\,\rho_1)$	(4)
at release	$I_2 = (M + M_0)\,(q_2 + x_2\,\rho_2)$	(5)
at compression	$I_3 = M_0\,(q_3 + x_3\,\rho_3)$	(6)

in which, q_0, q_1, q_2, q_3, and ρ_0, ρ_1, ρ_2, and ρ_3 are respectively the heats of the liquid, and the internal latent heats, or heat equivalents of the internal work, at the absolute pressures p_0, p_1, p_2, and p_3, measured on the indicator diagram, at admission, cut-off, release, and compression.

If the work under any line of the indicator diagram, reckoned from a perfect vacuum, is represented by W, and if A is the reciprocal of the mechanical equivalent of heat (equal to $\frac{1}{778}$), then the heat equivalents of the external work done by or on the piston are:

during admission	$A\ W_a$
during expansion	$A\ W_b$
during exhaust	$A\ W_c$
during expansion	$A\ W_d$

Usually heat is absorbed by the walls of the cylinder during admission of steam and up to the point of cut-off, heat is yielded

during expansion and during exhaust, while the interchange during compression is uncertain. It is possible that the walls may receive heat during expansion, and it is conceivable that they should give heat to the steam during the entire cycle; consequently it is convenient to affect all of the interchanges of heat by the same sign and to assume that heat absorbed by the wall is positive; in the solution of examples a negative sign will then mean that heat is yielded by the walls.

The interchanges of heat may be expressed as follows:

during admission	$Q_a = Q + I_0 - I_1 - A\,W_a$	(7)
during expansion	$Q_b = I_1 - I_2 - A\,W_b$	(8)
during exhaust	$Q_c = I_2 - I_3 - Mq_4 - G\,(q_k - q_i) + A\,W_c$ . .	(9)
during compression	$Q_d = I_3 - I_0 + A\,W_d$	(10)

In equation (9) the expression Mq_4 represents the heat carried away by the condensed steam flowing away from a surface condenser at the temperature t_4, and $G\,(q_k - q_i)$ represents the heat carried away by G pounds of cooling water, which enters with the temperature t_i and leaves with the temperature t_k.

Let the volume of one pound of water in cubic feet be σ, and let the increase of volume due to vaporization be u, so that the volume of one pound of dry steam is $u + \sigma$, while the volume of one pound of moist steam is $xu + \sigma$. Let the volume of the clearance of the engine be V_0 cubic feet, and let the volume developed by the piston at cut-off and release be V_1 and V_2, while the volume remaining at compression is $V_3 + V_0$. The volumes of the mixed fluid in the cylinder are:

at admission	$V_0 = M_0\,(x_0\,u_0 + \sigma)$	(11)
at cut-off	$V_0 + V_1 = (M + M_0)\,(x_1\,u_1 + \sigma)$	(12)
at release	$V_0 + V_2 = (M + M_0)\,(x_2\,u_2 + \sigma)$	(13)
at compression	$V_0 + V_3 = M_0\,(x_3\,u_3 + \sigma)$	(14)

An examination of the three groups of equations, (3) to (6), (7) to (10), and (11) to (14), will show that all that is requisite for an entire solution of our problem is the knowledge of the quality of the steam at one of the four events of the cycle. It is customary to assume the steam at compression to be dry and saturated, or that x_3 is unity. Such an assumption gives for the weight of steam weight at compression,

$$M_0 = \frac{V_0 + V_3}{u_3 + \sigma} = (V_0 + V_3)\,\gamma_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

in which γ_3 is the density or weight of one cubic foot of saturated steam at the absolute pressure at the beginning of compression.

Applying this result to equations (11) to (13) gives :

$$x_0 = \frac{V_0}{M_0 u_0} - \frac{\sigma}{u_0} \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (16)$$

$$x_1 = \frac{V_0 + V_1}{(M + M_0) u_1} - \frac{\sigma}{u} \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (17)$$

$$x_2 = \frac{V_0 + V_2}{(M + M_0) u_2} - \frac{\sigma}{u_2} \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (18)$$

Having the quality of the steam at admission, cut-off, and release, the several values of I at these points and at compression may be found from equations (3) to (6), and finally the interchanges of heat may be calculated by aid of equations (7) to (10). It may happen that the assumption of dry steam at compression may make the steam in the cylinder at admission appear to be superheated, *i.e.*, x_0 will appear to be larger than unity ; in such case it will be convenient to assume the steam to be saturated at admission also. The superheating is commonly small, and the error from the assumption of dry steam at compression and at admission is believed to be insignificant. In some of the tests to be quoted later the steam in the intermediate and low-pressure cylinders is superheated at release by the action of jackets supplied with steam at the boiler pressure. In such case the intrinsic energy of one pound of superheated steam may be calculated by aid of the equation [1]

$$E = 3pv + 778 \times 857.2 \quad \ldots \ldots \ldots \ldots \ldots \ldots \quad (19)$$

in which v is the specific volume in cubic feet, and p is the pressure in pounds on the square foot. Which will give at release

$$I_2 = (V_0 + V_2) \frac{3 \times 144\, p_2}{778} + 857.2\,(M + M_0) \quad \ldots \ldots \ldots \quad (20)$$

in which p_2 is the absolute pressure per square inch at release.

Let the heat lost by radiation, condensation, etc., be Q_e, and let Q_j be the heat supplied by the steam jacket when one is used. If the jacket is supplied by a separate pipe, or if in any way the water condensed therein can be withdrawn and measured, the value of Q_j is readily determined for any test ; Q_e may be determined by collecting the condensation in the jackets while the engine is at rest.

[1] Thermo-dynamics of the Steam Engine, p. 123, by the author.

Of the heat supplied to the cylinder per stroke, a part is changed into work, a part is carried away by the condensed steam and the cooling water, and the remainder is lost by radiation ; therefore

$$Q_e = Q + Q_f - Mq_4 - G(q_2 - q_1) - A\,W \quad \ldots\ldots\ldots\ldots \quad (21)$$

in which W is the work represented by the area of the indicator diagram, or

$$W = W_a + W_b - W_c - W_d \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (22)$$

Equation (21) may be used to calculate Q_e when it cannot be determined directly ; but such a calculation is vitiated by all the errors of determining the several quantities in that equation. When Q_e is determined directly, equation (21) may be considered a check on the accuracy of the determination of all the quantities appearing in it ; it is not a check on the determination of the interchanges by equations (7) to (10).

If a test is made on a non-condensing engine, or if for any reason the terms depending on the condenser cannot be determined, then these terms may be eliminated from equation (9) by aid of equation (21), giving

$$Q_e = I_2 - I_3 - Q - Q_f + Q_e + A\,(W + W_c) \quad \ldots\ldots\ldots \quad (23)$$

It may be of interest to note that this equation is equivalent to Hirn's direct determination of the exhaust waste, and that equation (9) is equivalent to his second determination or check. It is hardly necessary to call attention to the fact that such a check appears much more striking in an arithmetical calculation than in the algebraic statement of the analysis. Exception must be taken to the idea that the exhaust waste can be considered as a test of the efficiency of an engine. While it is true that a large exhaust waste causes a poor economy, the extinction of the exhaust waste, by lavish use of steam jackets or otherwise, may be dearly bought. This is well shown by Mair's tests.

COMPOUND ENGINES.

The equations (7), (8), and (10), with equation (23), may be applied directly to the high-pressure cylinder of a compound engine, giving :

$$Q_a = Q + I_0 - I_1 - A\,W_a \quad \ldots\ldots\ldots\ldots\ldots \quad (24)$$

$$Q_b = I_1 - I_2 - A\,W \quad \ldots\ldots\ldots\ldots\ldots \quad (25)$$

$$Q = I_2 - I_3 - Q - Q_f + Q_e + A\,(W + W_c) \quad \ldots\ldots \quad (26)$$

$$Q_d = I_3 - I_0 + A\,W_d \quad \ldots\ldots\ldots\ldots\ldots \quad (27)$$

By aid of equation (21) the term Q may be eliminated from the equation for the interchange of heat during admission; the other equations, (8) to (10), can be used unchanged in form. The interchanges of heat in the low-pressure cylinder can then be found by the equations:

$$Q'_a = Q'_e - Q'_f + Mq_4 + G(q_k - q_i) + I_0 - I_1 + A(W' - W'_a) \quad (28)$$

$$Q'_b = I'_1 - I'_2 - A W'_b \quad (29)$$

$$Q'_c = I'_2 - I'_3 - Mq - G(q_k - q_i) + A W'_c \quad (30)$$

$$Q'_d = I'_3 - I'_0 + A W'_d \quad (31)$$

These equations may be applied to any compound engine, whether it has a receiver or not, and without taking account of the loss or gain of heat experienced by the steam passing from the high to the low pressure cylinder. Thus it may be applied when there is a reheater between the cylinders, even though the heat thus imparted is not determined. It is apparent that this method cannot be extended to a triple-expansion engine.

MULTIPLE-EXPANSION ENGINES.

For multiple-expansion engines, the following method may be used. The heat rejected by the high-pressure cylinder during exhaust is

$$Q + Q_f - A W - Q_e \quad (32)$$

This heat passes into the first intermediate cylinder, and from there, with the gain or loss experienced, proceeds to the next cylinder. The sum, or difference, may be taken for Q'_1 the heat brought into the next cylinder per stroke. The same operation may be applied to each successive cylinder, and the final result may be checked by aid of the data depending on the condenser.

Compound and multiple-expansion engines, having various arrangements of steam-jackets and reheaters, will require special modifications of the form of the analysis. If two or more steam-jackets have a common drain, or if steam is passed in succession through several jackets, then the distribution of the heat among the several jackets must be determined or estimated.

The equations for the interchanges of heat in the triple engine of the Massachusetts Institute of Technology are as follows, the terms

Q_{eR} and Q_{jR} representing the heat radiated from the surface of an intermediate receiver and the heat supplied by condensation of steam in the jacket of such a receiver:

High-pressure cylinder,

$$Q = M(xr + q) \quad (33)$$
$$Q_a = Q + I_0 - I_1 - A\,W_a \quad (34)$$
$$Q_b = I_1 - I_2 - A\,W_b \quad (35)$$
$$Q_c = I_2 - I_3 - Q - Q_j + Q_e + A\,(W + W_c) \quad (36)$$
$$Q_d = I_3 - I_0 + A\,W_d \quad (37)$$

Intermediate cylinder,

$$Q' = Q + Q_j - A\,W - Q_e + Q_{jR} - Q_{eR} \quad (38)$$
$$Q'_a = Q' + I'_0 - I'_1 - A\,W'_a \quad (39)$$
$$Q'_b = I'_1 - I'_2 - A\,W'_b \quad (40)$$
$$Q'_c = I'_2 - I'_3 - Q' - Q'_j + Q'_e + A\,(W' + W'_c) \quad (41)$$
$$Q'_d = I'_3 - I'_0 + A\,W'_d \quad (42)$$

Low-pressure cylinder,

$$Q'' = Q' + Q'_j - A\,W' - Q'_e + Q'_{jR} - Q'_{eR} \quad (43)$$
$$Q''_a = Q'' + I''_0 - I''_1 - A\,W''_a \quad (44)$$
$$Q''_b = I''_1 - I''_2 - A\,W''_b \quad (45)$$
$$Q''_c = I''_2 - I''_3 - Q'' - Q''_j + Q''_e + A\,(W'' + W''_c) \quad (46)$$

or
$$Q''_c = I''_2 - I''_3 - M_{q4} - G\,(q_k - q_i) + A\,W''_d \quad (47)$$
$$Q''_d = I''_b - I''_0 + A\,W''_d \quad (48)$$

Finally,

$$\Sigma\,Q_e = Q_e + Q_{eR} + Q'_e + Q'_{eR} + Q''_e = Q + Q_j + Q_{jR} + Q'_j + Q'_{jR} + Q''_j - M_{q4} - G\,(q_k - q_i) - A\,(W + W' + W'') \quad (49)$$

APPLICATION OF ANALYSIS TO INSTITUTE OF TECHNOLOGY ENGINE.

The experimental engine in the engineering laboratories of the Massachusetts Institute of Technology is a three-crank horizontal triple-expansion engine with two intermediate receivers, built by E. P. Allis & Co., of Milwaukee. The receivers and the cylinders are thoroughly steam-jacketed by separate pipes from the main steam-pipe,

and drain individually into five receptacles for gathering and measuring the condensation. The jackets on the heads and barrels of the cylinders can be applied separately or together. Reducing valves are arranged to supply the jackets of the second receiver and the intermediate and low-pressure cylinder with steam at less than boiler pressure. The cranks are usually set 120° apart, the high-pressure crank leading, but the angle between the cranks can be varied. Steam is supplied to the engine through a 6-inch pipe carried under ground about 1,000 feet from the Rogers Building. Condensation is withdrawn from the pipe when it enters the building, and for further precaution the steam is passed through a Stratton separator on the way to the engine. The quality of the steam is determined near the throttle-valve by a throttling calorimeter. The exhaust from the engine is led to a surface condenser, beneath which is a Blake direct-acting air pump which discharges the condensed steam in weighing tanks. The automatic governor is arranged to control the cut-off of any or all of the cylinders; or, when the automatic gear is disconnected, the cut-off may be varied by hand. During all of the tests the governor controlled the cut-off of the high-pressure cylinder, and the cut-off on the other cylinders was adjusted to give expansion down to the back-pressure line in the high-pressure and intermediate cylinders. The low-pressure cylinder has two wrist-plates, so that the cut-off may be made longer than half stroke. The piping of the engine is arranged so that it may be run in several combinations; before making a test or series of tests all valves are arranged and tested to guard against leakage.

The main dimensions of the engine are as follows:

Diameter of the high-pressure cylinder	9	inches.
Diameter of the intermediate cylinder	16	"
Diameter of the low-pressure cylinder	24	"
Diameter of the piston-rods	$2\frac{3}{16}$	"
Stroke	30	"

Clearance in per cent. of the piston displacements:

High-pressure	cylinder,	head end,	8.83;	crank end,	9.76
Intermediate	"	"	10.4	"	10.9
Low-pressure	"	"	11.25	"	8.84

The following table gives the data and results of some tests made for the application of Hirn's analysis, by the class graduating this year:

	I.	II.	III.	IV.
Duration of test, minutes	60	60	60	60
Total number of revolutions	5299	5228	5173	5148
Revolutions per minute	88.3	87.1	86.2	85.8
Steam consumption during test, pounds:				
Passing through cylinders	1193	1157	1234	1305
Condensation in h. p. jacket	57	50	29	30
" in first receiver jacket	61	64	69	72
" in inter. jacket	85	92	97	105
" in second receiver jacket	53	50	52	51
" in l. p. jacket	89	76	90	87
Total	1538	1489	1571	1650
Condensing water for test, pounds	22847	22186	20244	20252
Priming, by calorimeter	0.013	0.012	0.011	0.012
Temperatures, Fahrenheit:				
Condensed steam	95.4	92.1	102.4	105.3
Condensing water, cold	41.9	42.1	43.0	42.8
Condensing water, hot	96.1	96.6	106.3	109.6
Pressure of the atmosphere, by the barometer, pounds per square inch	14.8	14.8	14.7	14.7
Boiler pressure, pounds per square inch, absolute	155.3	155.5	156.9	157.7
Vacuum in condenser, inches of mercury	25.0	25.1	24.1	23.9
Events of the stroke:				
High-pressure cylinder —				
Cut-off, crank end	0.192	0.194	0.245	0.283
head end	0.215	0.205	0.271	0.305
Release, both ends	1.00	1.00	1.00	1.00
Compression, crank end	0.05	0.05	0.04	0.04
head end	0.05	0.05	0.05	0.05
Intermediate cylinder —				
Cut-off, both ends	0.29	0.29	0.29	0.29
Release, both ends	1.00	1.00	1.00	1.00
Compression, crank end	0.03	0.03	0.03	0.03
head end	0 04	0.04	0.04	0.04
Low-pressure cylinder —				
Cut-off, crank end	0.38	0.38	0.38	0.38
head end	0.39	0.39	0.39	0.39
Release, both ends	1.00	1.00	1.00	1.00

	I.	II.	III.	IV.
Absolute pressures in the cylinder, pounds per square inch:				
High-pressure cylinder —				
Cut-off, crank end	145.9	145.9	138.8	138.3
head end	143.2	143.1	140.3	140.6
Release, crank end	41.3	41.5	44.7	48.4
head end	41.5	40.5	45.7	49.8
Compression, crank end	43.7	45.3	48.5	53.2
head end	48.7	47.9	54.5	62.0
Admission, crank end	64.5	68.8	72.2	81.2
head end	75.3	74.8	86.7	97.8
Intermediate cylinder —				
Cut-off, crank end	37.2	37.6	38.6	40.9
head end	35.0	35.3	39.6	42.6
Release, crank end	13.6	14.2	14.7	16.0
head end	13.4	13.8	14.9	16.0
Compression, crank end	16.3	17.3	18.2	19.0
head end	17.9	18.8	20.3	22.4
Admission, crank end	20.4	20.8	22.2	23.1
head end	21.1	22.8	24.2	26.7
Low-pressure cylinder —				
Cut-off, crank end	12.1	12.6	12.4	13.2
head end	12.0	12.4	13.1	14.0
Release, crank end	5.6	5.3	5.1	5.7
head end	5.4	5.8	5.9	6.4
Compression and admission —				
crank end	3.7	3.8	4.1	4.2
head end	4.3	4.5	4.6	4.7
Heat equivalents of external work, B. T. U. from areas on indicator diagram to line of absolute vacuum:				
High-pressure cylinder —				
During admission, $A\ W_a$, crank end	5.71	5.78	7.00	8.19
head end	6.61	6.37	8.42	9.50
During expansion, $A\ W_b$, crank end	10.65	10.76	10.40	10.25
head end	10.81	11.04	11.22	11.09
During exhaust, $A\ W_c$, crank end	7.73	7.89	8.44	9.02
head end	8.08	8.15	9.04	9.66
During compres'n, $A\ W_d$, crank end	0.48	0.60	0.49	0.50
head end	0.62	0.64	0.73	0.81
Intermediate cylinder —				
During admission, $A\ W_a$, crank end	7.58	7.57	7.98	8.64
head end	7.43	7.55	8.46	9.10
During expansion, $A\ W_b$, crank end	9.54	9.54	9.91	10.64
head end	9.22	9.31	10.37	11.14

	I.	II.	III.	IV.
Intermediate cylinder —				
During exhaust, $A\ W_c$, crank end	9.27	9.47	9.64	10.54
head end	9.27	9.47	10.18	10.84
During compres'n, $A\ W_d$, crank end	0.39	0.43	0.57	0.46
head end	0.60	0.70	0.78	0.84
Low-pressure cylinder —				
During admission, $A\ W_a$, crank end	7.75	7.95	8.33	8.97
head end	7.99	8.19	8.66	9.39
During expansion, $A\ W_b$, crank end	6.83	7.10	6.86	7.45
head end	6.87	7.12	7.34	7.87
During exhaust, $A\ W_c$, crank end	5.08	5.08	4.62	5.09
head end	5.08	5.16	4.81	5.00
During compres'n, $A\ W_d$, crank end	0.00	0.00	0.00	0.00
head end	0.00	0.00	0.00	0.00
Quality of the steam in the cylinder. At admission and at compression the steam was assumed to be dry and saturated:				
High-pressure cylinder —				
At cut-off . . . . . x_1	0.785	0.784	0.848	0.875
At release . . . . . x_2	0.899	0.903	0.920	0.931
Intermediate cylinder —				
At cut-off . . . . . x_1	0.899	0.912	0.906	0.908
At release . . . . . x_2	0.994	superheated.	superheated.	superheated.
Low-pressure cylinder —				
At cut-off . . . . . x_1	0.978	superheated.	0.970	0.974
At release . . . . . x_2	superheated.	superheated.	superheated.	superheated.
Interchanges of heat between the steam and the walls of the cylinders, in B. T. U. Quantities affected by the positive sign are absorbed by the cylinder walls; quantities affected by the negative sign are yielded by the walls:				
High-pressure cylinder —				
Brought in by steam . . . Q	132.93	130.77	141.11	149.84
During admission . . . Q_a	23.54	23.43	17.49	14.93
During expansion . . . Q_b	−18.69	−19.28	−15.33	−14.03
During exhaust . . . Q_c	−8.36	−7.22	−3.50	−2.38
During compression . . . Q_d	0.45	0.51	0.49	0.52
Supplied by jacket . . . Q_J	4.56	4.08	2.39	2.50
Lost by radiation . . . . Q_e	1.50	1.52	1.54	1.54
First intermediate receiver —				
Supplied by jacket . . . Q_{JR}	4.92	5.20	5.67	5.95
Lost by radiation . . . . Q_{eR}	0.58	0.58	0.59	0.59

	I.	II.	III.	IV.
Intermediate cylinder —				
Brought in by steam . . . Q' . .	131.89	129.61	137.87	146.64
During admission . . . . Q'_a . .	13.62	11.74	11.33	11.75
During expansion . . . Q'_b . .	−18.65	−18.84	−20.30	−21.88
During exhaust . . . . Q'_c . .	0.22	1.57	2.88	3.41
During compression . . . Q'_d . .	0.44	0.51	0.62	0.59
Supplied by jacket . . . Q'_j . .	6.82	7.50	7.97	8.64
Lost by radiation . . . . Q'_e . .	2.45	2.48	2.50	2.51
Second intermediate receiver —				
Supplied by jacket . . . Q'_{jR} .	4.20	4.04	4.27	4.22
Lost by radiation . . . Q'_{eR} .	1.20	1.22	1.23	1.24
Low-pressure cylinder —				
Brought in by steam . . Q'' . .	132.14	130.50	138.61	147.33
During admission . . . Q''_a . .	5.85	3.05	5.57	5.29
During expansion . . . Q''_b . .	−9.51	−7.09	−8.65	−10.13
During exhaust . . . . Q''_c . .	2.53	2.23	−1.44	−0.11
During compression . . . Q''_d . .	0.00	0.00	0.00	0.00
Supplied by jacket . . . Q''_j . .	7.08	6.20	7.41	7.14
Lost by radiation . . . Q''_e . .	4.34	4.40	4.45	4.47
Total loss by radiation:				
By preliminary test . . ΣQ_e . .	10.07	10.20	10.31	10.35
By equation (49)	11.68	10.19	8.75	8.07
Power and economy:				
Heat equivalents of works per stroke:				
High-pressure cylinder . AW . .	8.44	8.34	9.17	9.52
Intermediate cylinder . . AW' .	7.12	6.95	7.77	8.42
Low-pressure cylinder . AW'' .	9.64	10.06	10.87	11.79
Totals	25.20	25.35	27.81	29.73
Total heat furnished by jackets . . .	27.58	27.02	27.71	28.45
Distribution of work:				
High-pressure cylinder	1.00	1.00	1.00	1.00
Intermediate cylinder	0.84	0.83	0.85	0.88
Low-pressure cylinder	1.14	1.21	1.19	1.24
Horse-power	104.9	104.2	113.1	120.3
Steam per horse-power per hour . . .	14.65	14.31	13.90	13.73
B. T. U. per horse-power per minute .	247	241	236	232

An investigation of the results in the table shows that the difference in economy depends on the cut-off of the high-pressure cylinder, which is at about $\frac{1}{6}$ stroke for the first two, and at about $\frac{1}{4}$ stroke for the last two. The quantities that are most notably affected by the change of cut-off are the heat furnished by the high-pressure jacket and the condition of the steam, and interchanges of heat in the high-pressure cylinder. Thus the heat supplied by the high-pressure jacket for the tests, with the cut-off at $\frac{1}{4}$ stroke, is about half that furnished in the tests at $\frac{1}{6}$ stroke; which finds explanation or confirmation in the facts, that the steam is much dryer at cut-off with the longer cut-off, and that both the heat absorbed and yielded by the walls of the cylinder is notably less with that cut-off. The general accuracy and correctness of the tests is shown by the comparison of the total radiation, as found by collecting and weighing the jacket condensation when the engine was at rest, and by calculating the same by aid of the terms depending on the condenser. As has already been pointed out, this does not serve as a check on the interchanges of heat, but the regularity of the results for the intermediate and low-pressure cylinders must be considered to be very satisfactory, especially when it is remembered that any error made in work on the high-pressure and intermediate cylinders is carried on through all the remainder of the test. It may not be out of place to call attention to the fact that the four tests were made by four divisions of the class, and to say that carelessness or inaccuracy of a single observer might readily derange all the results of the test.

It is notable that the steam becomes dryer in its course through the engine, under the influence of the thorough steam-jacketing, with steam at boiler pressure, and that it is practically dry at release, in both the intermediate and low-pressure cylinders. In some of the tests it appears to be superheated at this point, and in one, even at cut-off in the low-pressure cylinder. The superheating is in no case large, and as it is accompanied by a small positive value for Q_c, the exhaust-waste, it may be that the steam was really dry and saturated at those points, though superheating by jackets filled with steam at so high a pressure is not impossible. Since a positive value for Q_c indicates that the walls absorbed heat during exhaust, such a result, if large, would be absurd; but in these tests it may properly be looked upon as the error, being in no case larger than about two per cent. of

the value of Q; if the steam at release is either dry or superheated, the value of Q must be very small or zero.

It is most remarkable that the heat furnished by the jackets is nearly as large in amount as that changed into work in the tests with the cut-off at $\frac{1}{4}$ stroke, and is actually larger for the tests with the cut-off at $\frac{1}{5}$ stroke. Also, that the heat lost by radiation is one third as much as the heat changed into work, if not more; the engine being arranged for convenient experimental work, probably has a large radiation, though it is thoroughly wrapped and lagged on all hot surfaces.

ON THE DETERMINATION OF THE ELECTROLYTIC DISSOCIATION OF SALTS BY MEANS OF SOLUBILITY EXPERIMENTS.

By ARTHUR A. NOYES, Ph.D.

Contents. — 1. General theory of solubility effect. 2. Special case where the two salts have one ion in common. 3. Solubility experiments a method of determining dissociation. Purpose of this investigation. 4. Description of the experiments. 5. Experiments with thallous chloride and the alkali chlorides. 6. Dissociation of the alkali chlorides. 7. Experiments with thallous chloride and hydrochloric acid. 8. Dissociation of hydrochloric acid. 9. Experiments with thallous chloride and thallous nitrate and chlorate. Dissociation of the last two salts. 10. Experiments with thallous chloride and magnesium, calcium, barium, copper, zinc, and manganese chlorides. 11. Dissociation of these bivalent-metal chlorides. 12. Experiments with thallous chloride and cadmium chloride; dissociation of the latter. 13. Experiments with thallous chloride and mercuric and lead chlorides. 14. Experiments with lead chloride and potassium, magnesium, calcium, manganese, zinc, and cadmium chlorides, and hydrochloric acid. 15. Theory of solubility effect between two ternary electrolytes. 16. Experiments with lead chloride and mercuric chloride and lead nitrate. 17. Conclusion.

1. GENERAL THEORY OF SOLUBILITY EFFECT.

The effect which one salt exerts on the solubility of another has been the subject of numerous and extended investigations. These yielded, however, nothing more than a mass of empirical results, until two years ago, when it was shown by Nernst[1] that the electrolytic dissociation theory offered an explanation of this phenomenon of solutions, as it had already done of so many others. The bearing of this theory on the matter of solubility will be evident from the following considerations:

A saturated solution is to be regarded as a condition of equilibrium between the undissolved substance on the one hand, and the portion of it dissolved in the solvent on the other. It is, moreover, a condition of equilibrium independent of the amount of the solid body in contact

[1] Zeitschrift für physikalische Chemie, 4, 372.

with the solution — a fact ordinarily expressed by saying that the active mass of the undissolved substance is constant. The active mass of the dissolved portion, which holds the equilibrium with this, must likewise be constant as long as the temperature, the solvent, and the chemical nature of the dissolved substance remain unchanged. Although this statement seems self-evident, yet, before the establishment of the electrolytic dissociation theory, it could not be consistently maintained. For it was frequently observed that the solubility of a salt was greatly influenced by the addition of another, even in cases where a chemical reaction between them seemed impossible, and where the small quantity of the second substance added made the assumption of an essential change in the nature of the solvent very improbable; and there was at that time no reason to regard the active mass in the solution as anything else than the total quantity of dissolved substance. The electrolytic dissociation theory, however, has shown that salts, acids, and bases, in aqueous solution, undergo a partial, often nearly complete, dissociation into their electrolytic components or ions. A dilute solution of sodium chloride, or of nitric acid, for example, contains comparatively few molecules of the composition NaCl or HNO_3, but these have been broken up by the act of solution into $\overset{+}{Na}$ and $\overset{-}{Cl}$, or $\overset{+}{H}$ and $\overset{-}{NO_3}$, ions, which exist as molecules chemically independent of each other. Returning now to the case of a saturated solution, it is clear in the light of this theory that the total quantity of dissolved substance has entirely lost its chemical significance as an active mass: that which in the solution does hold the equilibrium with the undissolved substance is either the ions or the undissociated portion of the salt, or most probably both together. Which of these three possibilities is actually the case does not concern us; for, according to the general law of dissociation, the active mass of the undissociated substance in the solution must be proportional to the product of the active masses of its dissociation products, in this case the ions. If, now, as in a saturated solution, the system is so conditioned that one of these quantities is constant, it follows that the other must be so likewise. The following two principles may therefore be laid down as the basis of the theory of solubility effect:

1. In a saturated solution of a partly dissociated substance, the undissociated portion remains unchanged in quantity, even though a second dissociated substance be added.

2. The product of the active masses of the dissociation products (the ions) of the substance with which the solution is saturated remains constant also.

The validity of these principles depends on two conditions: first, that the addition of the second substance be not so great nor of such a nature as to cause a sensible change of the solvent; and second, that no special chemical action between the dissolved substances, like, for example, the formation of a double salt, comes into play.

2. SPECIAL CASE WHERE THE TWO SALTS HAVE ONE ION IN COMMON.

Let us consider the case where one of the ions of the substance added is identical with one of those of the body with which the solution is saturated; for example, suppose hydrochloric acid added to a saturated solution of potassium chloride. By this addition a new quantity of chlorine ions is brought into the solution; therefore, in order that the product of the quantities of potassium and chlorine ions may remain constant, the quantity of the potassium ions must decrease; in other words, potassium chloride is precipitated — its solubility is diminished. This case is completely analogous with dissociation in the gaseous condition; for example, the introduction into a space saturated with ammonium chloride vapor of one of its decomposition products, ammonia or hydrochloric acid gas, causes, as is well known, a condensation of a portion of the salt.

As the mathematical expression for the influence on the solubility in the case of binary electrolytes, Nernst gives the following formula:

$$m_0^2 a_0^2 = ma\,(ma + xa_1);$$

in which m_0 denotes the solubility of the body in pure water; m, its solubility after the addition of the quantity x of another substance with one of the same ions; a_0, the dissociation of the first substance in saturated solution before the addition; a, its dissociation after the addition of the second substance; and a_1 the dissociation of the latter. This formula is the expression of the second principle given above; it states the constancy of the product of the quantities of the two ions; for $m_0 a_0$ is plainly the quantity of each of them before the addition of the second salt; ma is the quantity of the ion not added, and $(ma + xa_1)$, that of the added ion, after the addition.

As expression of the first principle of solubility effect, which has reference to the undissociated portion, we have the following simple formula:

$$m_0 (1 - a_0) = m (1 - a).$$

Solving these two equations for m, we get:

$$m = -\frac{xa_1}{2a} + \sqrt{m_0^2 \frac{a_0^2}{a^2} + \frac{x^2 a_1^2}{4a^2}}$$

$$m = m_0 \frac{1 - a_0}{1 - a}$$

It is evident that by means of these formulæ, from the solubility of a salt in pure water, its solubility in the presence of any added amount x of another salt can be calculated, provided the degrees of dissociation (a_0, a_1, and a) of the two salts are known. The dissociation of a salt, however, may be determined, at least approximately, by taking the ratio of the molecular electrical conductivity of its solution at the concentration in question, to its molecular conductivity at extreme dilution,[1] where it is completely dissociated. It was the special object of an investigation which I made last year,[2] to test Nernst's theory of solubility above described; and it was, in fact, proved by experiments with eleven different pairs of salts that the results calculated by means of this theory are in quite close agreement with those experimentally obtained. Differences, however, did occur, which were undoubtedly far greater than the experimental errors; they lay, moreover, always in the same direction. There is good reason to believe that the cause of these deviations is the incorrectness of the values of the dissociation used in the calculation; that is to say, that it lies in the inaccuracy of the assumption that dissociation and molecular conductivity are exactly proportional, and not in the invalidity of the laws of chemical mass action, which are the basis of the theory of solubility effect.

[1] Arrhenius, Zeitschrift für physikalische Chemie, 1, 632.

[2] Zeitschrift für physikalische Chemie, 6, 241.

To give an idea of the magnitude of these differences, I tabulate below the results of two series of experiments described in my previous article :

$AgBrO_3$ with $AgNO_3$ and $KBrO_3$ (24.5°).

Added Quantity.	Solubility in the presence of $AgNO_3$	Solubility in the presence of $KBrO_3$	Calculated Solubility.
0	0.00810	0.00810	. . .
0.00850	0.00510	0.00519	0.00504
0.0346	0.00216	0.00227	0.00206

$TlCl$ with $TlNO_3$ and HCl (25°).

Added Quantity.	Solubility in the presence of $TlNO_3$.	Solubility in the presence of HCl.	Calculated Solubility.
0	0.0161	0.0161	. . .
0.0283	0.00830	0.00836	0.00783
0.0560	0.00571	0.00565	0.00508
0.1468	0.00332	0.00316	0.00253

3. SOLUBILITY EXPERIMENTS A METHOD OF DETERMINING DISSOCIATION. PURPOSE OF THIS INVESTIGATION.

This discrepancy between the observed and calculated values of the solubility suggested the application of solubility experiments as an independent method of determining the dissociation of salts ; for, just as the solubility m of one salt in the presence of another can be calculated, if the values of the dissociation are known, so conversely can the degree of dissociation be determined from the values of the solubility experimentally obtained. Of the various physical properties of solutions which are dependent on the dissociation of the dissolved substance, the electrical conductivity is the only one which, up to the present time, has furnished any accurate measure of it. Other properties, like the freezing point and the vapor pressure, differ, in the case of dilute solutions, so little from those of the pure solvent, that the experimental errors make them properties of little value in the determination of the dissociation ; while for concentrated solutions they give inaccurate results, owing to the deviation from the law of Avo-

gadro in their case. From the electrical conductivity of their solutions, the dissociation of a very large number of organic acids has been determined by Ostwald and others, and the values so obtained varied with the concentration in almost all cases in the manner required by the general laws of dissociation; which fact alone is very strong evidence of their accuracy. In the case of the better conductors, however, like most salts, strong acids and bases, the dissociation indicated by the conductivity does not change in accordance with the laws of dissociation; but it decreases with the increase of concentration much more slowly than those laws require, which is itself an indication of incorrectness. Especially after I had found that the solubility effect indicated a smaller dissociation in the more concentrated solutions than that deduced from the conductivity, did there exist strong reasons for doubting the exact proportionality between dissociation and conductivity, and for giving greater confidence to the results of solubility experiments.

These considerations, and the great importance of an accurate knowledge of the dissociation constants in all applications of the theory of electrolytic dissociation, led me to undertake the present investigation, which has for its special object the study of the dissociation of the chlorides of the various metals.

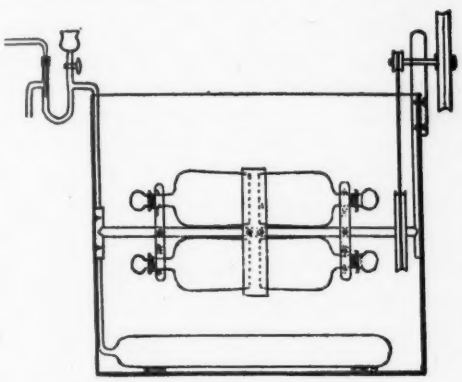
4. DESCRIPTION OF THE EXPERIMENTS.

Two series of experiments were made, in one of which thallous chloride, and in the other of which lead chloride was taken as the substance with which the solution was saturated; and the solubility of each of these two compounds in solutions containing different known quantities of the various metallic chlorides was determined.

A 0.2 normal and a 0.05 normal solution of each of the chlorides whose effect on the solubility was to be determined, were prepared by weighing out the solid substances when this was practicable, and by titration of the solutions with silver nitrate when it was not. Exactly 100 cc. of each of these solutions were placed in a small bottle, and an excess of the thallous or lead chloride was added in the form of a fine, dry powder. The bottles were closed with tightly fitting cork stoppers, and placed in a bath kept at a constant temperature by means of a regulator of the kind described by Ostwald.[1] All experi-

[1] Zeitschrift für physikalische Chemie, 2, 564.

ments were made at a temperature of 25°. In order to secure continuous agitation, and thereby rapid saturation, a machine was constructed in the manner illustrated in the accompanying sketch.



A horizontal brass shaft, set in bearings within the thermostat, had soldered to it at its middle point two annular metal bands of such diameter that the bottoms of the bottles to be rotated just fitted into them. In order to keep the bottles firmly in their horizontal position, the neck of each was clasped between two elastic pieces of metal attached to the shaft near its ends. Four bottles were in this way provided for, and, by means of rubber bands passing around them, four more could be fastened to the shaft, so that eight were easily rotated at one time. A rubber belt passing over a wheel near the end of the shaft, and over a second smaller wheel on a horizontal axle at the top of the thermostat, served to transfer the power from a small electric motor. The shaft made about twenty revolutions per minute; and the agitation of the solutions was sufficient to keep the finer particles of the solid substances in suspension, while the coarser particles rolled along the sides of the bottle as it turned over and over. The solutions were rotated for three hours; the bottles were then detached from the shaft and placed in an upright position on a perforated shelf within the bath, where the solutions were allowed to settle for three to four hours. By means of a pipette 50 cc. of the clear solution were then taken out and submitted to analysis; 50 cc. of distilled water were then added to the 50 cc. remaining in the bottle, and the solution so obtained, containing the added substance in only half the previous concentration (0.1 or 0.025 normal), was ready for a second rotation. In the case of thallous chloride, experiments were made with four different dilutions: 0.2, 0.1, 0.05, and 0.025 normal; with lead chloride the last was omitted, owing to its much greater solubility.

5. EXPERIMENTS WITH THALLOUS CHLORIDE AND THE ALKALI CHLORIDES.

The substances whose effect on the solubility of thallous chloride was first tried were the chlorides of the alkalies, potassium, sodium, and ammonium. The potassium and sodium chlorides used were prepared from the commercial chemically pure salts by precipitation of the solutions with hydrochloric acid and subsequent ignition of the precipitate; the ammonium chloride was purified by precipitation and subsequent sublimation.

As the experiments in contemplation involved the making of more than a hundred thallium determinations, it was highly desirable, in fact almost indispensable, to find a simple volumetric method. Of the various processes which have been proposed, the titration with potassium permanganate, by which the thallous is converted to a thallic salt (Tl_2O to Tl_2O_3), was found to be by far the most satisfactory. As this method, which was discovered by E. Willm,[1] seems to have been little used, and as it gives thoroughly reliable results, it will perhaps be well to describe it briefly.

A solution of permanganate, approximately $\frac{1}{25}$ normal, was standardized against thallous sulphate, which is easily obtained perfectly pure by crystallization, and which is anhydrous and not hygroscopic. About 0.1 of a gram of this is dissolved in water, the solution is diluted to 200 cc., 10 cc. of hydrochloric acid of 1.2 specific gravity are added, and the permanganate solution is added rather slowly till the slightest pink color is observable. The end point is exceedingly sharp, and the color persists for several minutes. The thallium solution must be diluted to the extent indicated, in order to avoid precipitation of thallous chloride. Within certain limits the amount of hydrochloric acid added is a matter of indifference; for example, it was found that with 12 cc. the end point was as sharp as with 10 cc. With 20 cc., however, the pink color of the end point disappeared quite rapidly, so that the results were unreliable. With 8 cc., the brown hydrated manganese dioxide separated towards the end of the titration. The presence of metallic chlorides was found by special experiments to have no influence on the result. This method of analysis was used in all cases where chlorides were added to the thallous chloride.

[1] Répertoire de chimie pure, 5, 352, (1863).

The results obtained with the three alkali chlorides are given in the following tables. The numbers indicate here, as throughout this article, the number of equivalents dissolved in a litre.

TABLE I. TlCl in the presence of KCl, NaCl, and NH_4Cl.

Salt added.	Its Concentration.	Solubility of TlCl.	Mean of Experiments.	Mean for the three Salts.
None.	0	0.01611[1]	. . .	. . .
. . .	. . .	0.01619[1]	. . .	. . .
. . .	. . .	0.01619[2]	0.01612	0.01612
. . .	. . .	0.01604[2]	. . .	. . .
. . .	. . .	0.01607[2]	. . .	. . .
KCl.	0.025	0.00871	0.00872	. . .
. . .	. . .	0.00872	. . .	. . .
NaCl.	. . .	0.00870	0.00869	0.00872
. . .	. . .	0.00868	. . .	. . .
NH_4Cl.	. . .	0.00876	0.00877	. . .
. . .	. . .	0.00878	. . .	. . .
KCl.	0.05	0.00591	. . .	. . .
. . .	. . .	0.00594	0.00593	. . .
. . .	. . .	0.00593	. . .	. . .
NaCl.	. . .	0.00593	0.00592	0.00592
. . .	. . .	0.00590	. . .	. . .
NH_4Cl.	. . .	0.00594	. . .	. . .
. . .	. . .	0.00589	0.00593	. . .
. . .	. . .	0.00597	. . .	. . .
KCl.	0.1	0.00400	0.00399	. . .
. . .	. . .	0.00398	. . .	0.00397
NaCl.	. . .	0.00395	0.00395	. . .
. . .	. . .	0.00394	. . .	. . .
KCl.	0.2	0.00267	0.00265	. . .
. . .	. . .	0.00263	. . .	. . .
NaCl.	. . .	0.00273	0.00271	0.00269
. . .	. . .	0.00268	. . .	. . .
NH_4Cl.	. . .	0.00269	0.00271	. . .
. . .	. . .	0.00273	. . .	. . .
KCl.	0.8	0.00170	0.00170	. . .

[1] Chlorine determined by Volhard's method. [2] Thallium determined by titration with potassium permanganate.

From these results it is evident that the three substances, potassium, sodium, and ammonium chlorides, have practically the same effect on the solubility of thallous chloride, and that this holds true for all the concentrations studied. It follows, therefore, at once, that these three chlorides are equally dissociated at the same concentrations; or, in other words, that they have the same dissociation constant.

6. DISSOCIATION OF THE ALKALI CHLORIDES.

Before, however, we can determine the absolute values of the dissociation of the added salt, it is necessary that we know something about that of the thallous chloride. For the diminution of the solubility of a salt depends on its own dissociation as well as on that of the added salt. Now, unfortunately, we have no accurate knowledge of the dissociation of thallous chloride; nevertheless, it is probable that it is dissociated to the same extent as the alkali chlorides, since the three univalent metal chlorides investigated agree so completely in this respect; and it seems especially so when the great similarity of the potassium and thallium salts is considered. It deserves mention, moreover, in this connection, that potassium, sodium, and thallous hydrates have been shown by Ostwald to be equally dissociated, for they saponify acetic ether at the same rate.[1]

At any rate, this very probable assumption has to be made preliminarily, and it is the basis of the calculations made in this article. If at any time more accurate knowledge is obtained of the dissociation of thallous chloride, the results can be corrected correspondingly. It will now be seen that in the calculation of the dissociation of the added salt this assumption suffices, no more specific knowledge of the dissociation of the thallous chloride being required.

The two equations deduced at the beginning of this article as the mathematical expression of the fundamental principles of solubility effect are:

$$m_0 (1 - a_0) = m (1 - a) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$m_0^2 a_0^2 = ma (ma + xa_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

These equations contain three unknown quantities, a_0, a, and a_1, and cannot, therefore, of themselves be solved. If, however, we make

[1] Journal für praktische Chemie, 35, 121. The constants representing the relative velocities of the reactions in the three cases are 161, 162, and 158, respectively. The solutions employed were rather dilute, however; viz., $\frac{1}{40}$ normal.

the assumption just discussed, that the dissociation constant C has the same value for the added and for the original salt, we have according to the laws of dissociation for the former,

$$C\,x\,(1-a_1) = xa_1\,(ma + xa_1),$$

and for the latter,

$$C\,m\,(1-a) = ma\,(ma + xa_1);$$

whence

$$\frac{a_1}{1-a_1} = \frac{a}{1-a}, \text{ or } a_1 = a.$$

That is, the dissociation of the added salt in the saturated solution of the original salt is the same as the dissociation of the latter in the solution of the former. Equation (2), therefore, becomes

$$m_0^2 a_0^2 = m^2 a_1^2 + mxa_1^2,$$

and combining this with equation (1) with elimination of a_0 and solving for a_1, we get

$$a_1 = \frac{m_0 - m}{x}\left(1 + \sqrt{1 + \frac{x}{m}}\right) \quad \ldots\ldots\ldots \quad (3)$$

by means of which the dissociation corresponding to the various concentrations can be calculated.

It is, however, to be observed that the dissociation a_1 is not the dissociation of the added quantity x in *pure water*, but is its dissociation in the presence of the quantity m of the salt with which the solution is saturated. In order to determine the concentration, y, of the salt in pure water to which the dissociation a_1 corresponds, consider the two dissociation formulæ,

$$C = \frac{xa_1\,(ma + xa_1)}{x\,(1-a_1)} \text{ and } C = \frac{y^2 a_1^2}{y\,(1-a_1)},$$

whence follows on combination,

$$y = x + m\,\frac{a}{a_1} \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

or, in the case under present consideration, where $a = a_1$, $y = x + m$.

In Table II are given the values of the dissociation calculated from the results of the foregoing table by formula (3). As the variations in the solubility effect of the three different salts are small and irregular, and probably due mainly to experimental error, only a single cal-

culation for each concentration has been made; and in this calculation the mean values of m given in the fifth column of Table I have been used. In the first column of the following table is given the value of x, the added quantity of the salt; in the second, that of $y = m + x$, the concentration of the salt in pure water, to which the dissociation a_1, given in per cent. in the third column, corresponds. In the fourth column, under C, is given the value of the dissociation constant $C = \frac{1 - a_1}{a_1^2 y}$. In the fifth, under 100 a_1 (calc.), is given the value of a_1 corresponding to the mean value of the constant 4.4. And in the sixth column is given a_0, the dissociation of the thallous chloride in saturated solution in pure water (concentration = 0.01612), calculated by means of formula (1) from each value of m and a_1.

TABLE II. Dissociation of KCl, NaCl, and NH_4Cl.

x.	y.	$100a_1$.	C.	$100a_1$ (calc.)	$100a_0$.
0.025	0.0337	87.8	4.7	88.4	93.4
0.050	0.0559	83.1	4.4	83.0	93.8
0.100	0.1040	74.3	4.5	74.6	93.7
0.200	0.2027	65.0	4.1	63.8	94.2

While the dissociation varies from 65 to 88 per cent., the value of the theoretical dissociation constant remains nearly the same. It is to be remembered that errors in the dissociation are greatly multiplied in the constant. A comparison of the figures of the fifth column, which are calculated from the mean value of the constant (4.4), with those of the third, gives a better idea than the constant itself of the degree of conformity with the law of dissociation. In the three diluter solutions the agreement is within seven tenths of a per cent., while in the most concentrated one, where the error in the dissociation, owing to the small solubility and to theoretical causes, is undoubtedly large, the variation amounts to about two per cent. The proof here given, that the laws of chemical mass action are applicable to electrolytic dissociation in the case of salts, forms one of the most important results of this investigation.

It is of especial interest to compare these values of the dissociation

and of the dissociation constant with those deduced from the electrical conductivity. In Table III the results by the two methods are placed side by side. Kohlrausch's[1] values of the conductivity of potassium chloride have been made the basis of the calculation of the dissociation, which is, as usual, assumed equal to the ratio $\left(\frac{\mu_v}{\mu_\infty}\right)$ of the molecular conductivity at any dilution v to that at extreme dilution. The dissociation deduced from the solubility experiments has been interpolated from the above results for the round concentration values, 0.03, 0.05, 0.1, and 0.2, with the help of the constant.

Table III. Comparison of the Dissociation of KCl as determined from the Electrical Conductivity and from Solubility Experiments.

Concentration.	(A). Dissociation from solubility effect.	(B). Dissociation from electrical conductivity.	Constant corresponding to (A).	Constant corresponding to (B).
0.016	93.8	93.3	(4.4)	4.8
0.03	88.7	91.0	4.7	3.6
0.05	84.3	89.1	4.4	2.8
0.1	74.8	86.1	4.5	1.9
0.2	65.2	82.8[2]	4.1	1.3

It is evident from the above table that the two methods lead to practically the same dissociation only for the greatest dilution (0.016 normal), and that in all the other cases considerable differences exist, which increase in magnitude as the concentration increases, and which reach at the greatest concentration (0.2 normal) the large amount 17.6 per cent. Further, the electrical conductivity gives values of the dissociation which are uniformly greater than those deduced from the solubility experiments, the differences thus agreeing in direction with those observed in all my previous experiments.[3]

The values of the dissociation constant in the two cases need little comment. The fact that the dissociation calculated from the

[1] Annalen der Physik und Chemie, **26**, 195.
[2] Graphically interpolated from Kohlrausch's plot.
[3] Compare Zeitschrift für physikalische Chemie, **6**, 249.

solubility effect changes with the dilution in the manner required by the laws of dissociation, while that calculated from the conductivity deviates greatly from it, is of itself strong proof of the correctness of the former.

The determination of the dissociation of salts from the electrical conductivity seems therefore no longer justified except for very dilute solutions. It has always been supposed that this method was inapplicable for considerable concentrations; but Ostwald having shown its applicability up to $\frac{1}{8}$ normal in the case of many organic acids, it was assumed to be correct for equally strong solutions of salts and inorganic acids. It seems to me, however, that the results indicate that the limit of applicability of the method depends less on the concentration of the solution than on the concentration of the ions; in other words, that the electrical conductivity gives correct values of the dissociation as long as the number of ions does not exceed a certain comparatively small amount; which explains why organic acids, which are in general little dissociated, may be investigated by the method at much greater concentrations than more dissociated bodies like salts and strong acids.

The fact that the conductivity of the more concentrated solutions is greater than the dissociation of the dissolved substances justifies, is, I believe, to be explained by the participation of the water itself in the conduction; that is to say, water, which in a pure state contains only an excessively small number of ions, becomes appreciably dissociated when substances, especially electrolytes, are dissolved in it. In my previous article on solubility I did not venture to suggest this explanation, as there were no other facts to support it; but since then Le Blanc[1] has been led to the same assumption by his experiments on the minimum electromotive force required for the electrolysis of various solutions. This he found to have nearly the same value for a large number of dissimilar acids and bases, from which fact he concluded that the same substance, namely, the water, was being primarily electrolyzed in all these cases. Though the correctness of this hypothesis has not been fully proved, it must be admitted that the phenomena of electrolysis are explained much more simply and much more naturally by it than by the older, equally unproved hypothesis in which secondary actions play the principal part.

[1] Zeitschrift für physikalische Chemie, 8, 313.

7. EXPERIMENTS WITH THALLOUS CHLORIDE AND HYDROCHLORIC ACID.

The effect of hydrochloric acid on the solubility of thallous chloride was next investigated. The results are contained in the following table:

TABLE IV. TlCl in the presence of HCl.

Concentration.	Solubility of TlCl with HCl added.	Mean of Experiments.	Sol. of TlCl with KCl, NaCl, and NH_4Cl added.
0	. . .	0.01612	. . .
0.025	0.00870	0.00869	0.00872
. . .	0.00868	. . .	. . .
0.05	0.00586	0.00585	0.00592
. . .	0.00585	. . .	. . .
0.1	0.00384	0.00384	0.00397
. . .	0.00383	. . .	. . .
0.2	0.00255	0.00254	0.00269
. .	0.00254	. . .	. . .

Hydrochloric acid diminishes the solubility of thallous chloride to a somewhat greater extent than the alkali chlorides; the differences, however, are not very large. It is, therefore, dissociated to a slightly greater extent.

8. DISSOCIATION OF HYDROCHLORIC ACID.

In order to calculate its dissociation, we make use, as before, of formulas (1) and (2), which contain the three unknown quantities a_0, a_1, and a. But since a_1 and a are in this case not equal, equation (3), which results from their combination under that supposition, cannot be used. By the experiments already described, however, the value of a_0 has been determined, and is given in the last column of Table II, (mean value = 0.938). Equations (1) and (2) can now, therefore, be solved for a_1 and a, with the following result:

$$a_1 = \frac{2m_0 a_0 - (m_0 - m)}{x\left(\frac{m_0 a_0}{m_0 - m} - 1\right)} \quad \ldots\ldots\ldots\ldots (5).$$

$$a = \frac{(m_0 - m)^2}{m\left(xa_1 - 2(m_0 - m)\right)} \quad \ldots\ldots\ldots\ldots (6).$$

The concentration of the acid in pure water, y, to which the dissociation a_1 corresponds, is given by equation (4), as shown above.

TABLE V. Dissociation of HCl.

γ	0.0337	0.0557	0.1037	0.2021
$100\alpha_1$ (for HCl)	88.2	84.7	77.7	73.5
$100\alpha_1$ (for KCl)	87.8	83.1	74.3	65.0

Concentration.	(A). Dissociation from solubility effect.	(B). Dissociation from electrical conductivity.[1]	Constant corresponding to (A).	Constant corresponding to (B).
0.03	89.1	95.7	4.6	1.6
0.05	85.4	94.6	4.0	1.2
0.1	78.1	92.1	3.6	0.9
0.2	73.2	89.8[2]	2.5	0.6

The first table contains the values calculated directly from the experiments, and the second, those interpolated for the concentrations, 0.03, 0.05, 0.1, 0.2.

Here again the dissociation deduced from the solubility effect is much less than that deduced from the electrical conductivity, the differences being even considerably greater than those in the case of the alkali chlorides. The dissociation constant corresponding to the solubility values, though much better than that corresponding to the conductivity values, is not completely satisfactory. It is evident either that the laws of dissociation are not completely followed by hydrochloric acid at the concentrations considered, or that the assumption involved in the calculation that the solvent power of the dilute hydrochloric acid is the same as that of water, is not entirely correct. It is constantly to be remembered that this assumption, which is undoubtedly invalid for very concentrated solutions, may not be exactly true in the case of certain substances in diluter solutions. At any rate, the direction in which the constant changes, since it is undoubtedly more nearly correct for the diluter solutions, indicates that the dissociation cannot be greater than the values given, but is, if anything, less. There is thus no hope of a reconciliation with the conductivity values; and those from the solubility should, it seems to me, be regarded preliminarily as the more probable.

[1] Calculated from Kohlrausch's experiments, assuming $\mu_\infty = 352$.
[2] Interpolated from Kohlrausch's plot ($\mu_v = 316.2$).

9. EXPERIMENTS WITH THALLOUS CHLORIDE AND THALLOUS NITRATE AND CHLORATE. DISSOCIATION OF LAST TWO SALTS.

The thallous nitrate used was prepared by dissolving metallic thallium in nitric acid, and crystallizing the product from hot water. The thallous chlorate was made by double decomposition between thallous sulphate and barium chlorate. The amount of thallous chloride dissolved in the presence of each salt was found, not as before by a determination of the thallium, but by one of the chlorine, made volumetrically by Volhard's method in the case of the nitrate, and gravimetrically in the case of the chlorate.

TABLE VI. TlCl in the presence of $TlNO_3$ and $TlClO_3$.

Salt added.	Its Concentration.	Solubility of TlCl.	Dissociation of added salt ($100\,a_1$).	Corresponding concentration (y).	Dissociation Constant.
None.	0	0.01612	. . .	. . .	. . .
$TlNO_3$	0.025	0.00883	85.5	0.0342	5.8
. . .	0.05	0.00626	76.5	0.0569	7.1
. . .	0.1	0.00423	67.6	0.1048	6.8
$TlClO_3$	0.025	0.00897	83.2	0.0346	7.0
. . .	0.025	0.00894	. . .	. . .	. . .

The dissociation of these two salts is in all cases a little less than that of the alkali chlorides. The constant in the case of thallous nitrate shows irregular variations, probably due to experimental errors.[1]

10. EXPERIMENTS WITH THALLOUS CHLORIDE AND MAGNESIUM, CALCIUM, BARIUM, COPPER, ZINC, AND MANGANESE CHLORIDES.

The effect of the chlorides of a number of bivalent metals on the solubility of thallous chloride was next studied. The solution of magnesium chloride was prepared by treating metallic magnesium with an insufficient quantity of hydrochloric acid, decanting the solution which had become slightly alkaline, and neutralizing it with more acid. That

[1] The results with thallous nitrate are, I fear, less accurate than the others given in this article; for, though the experiments were many times repeated, closely agreeing resu ts were not obtained.

of calcium chloride was made by dissolving pure calcium carbonate in hydrochloric acid, adding a little lime to precipitate magnesium and other metals, filtering, and exactly neutralizing with hydrochloric acid. The commercial chemically pure salts were used in the case of barium and copper. The solution of zinc chloride was made by double metathesis between zinc sulphate and barium chloride. The manganese chloride was freed from iron after oxidation with chlorine by addition of manganese carbonate and recrystallization. In the case of barium chloride, the anhydrous salt was weighed out. In all the other cases the solution was diluted to exactly 0.2 normal with the help of a standard silver nitrate solution.

The thallium was determined with potassium permanganate as described above. In the case of the copper, owing to the blue color, that metal had to be removed by the addition of sodium hydrate before proceeding with the titration. The results are given in Table VII.

TABLE VII. TlCl in the presence of $MgCl_2$, $CaCl_2$, $BaCl_2$, $MnCl_2$, $ZnCl_2$, and $CuCl_2$.

Salt added.	Its Concentration.	Solubility of TlCl.	Mean of Experiments.	Mean for the six salts.
None.	0	. . .	0.01612	. . .
$MgCl_2$	0.025	0.00901	0.00904	. . .
$MgCl_2$	0.025	0.00908	. . .	. . .
$CaCl_2$	0.025	0.00898	0.00899	. . .
$CaCl_2$	0.025	0.00899	. . .	. . .
$MnCl_2$	0.025	0.00897	0.00898	0.00901
$MnCl_2$	0.025	0.00898	. . .	. . .
$ZnCl_2$	0.025	0.00897	0.00899	. . .
$ZnCl_2$	0.025	0.00901	. . .	. . .
$CuCl_2$	0.025	0.00904	0.00905	. . .
$CuCl_2$	0.025	0.00907	. . .	. . .
$MgCl_2$	0.05	0.00617	0.00618	. . .
$MgCl_2$	0.05	0.00618	. . .	. . .
$CaCl_2$	0.05	0 00623	0.00624	. . .
$CaCl_2$	0.05	0.00626	. . .	. . .
$BaCl_2$	0.05	0.00618	0.00620	. . .
$BaCl_2$	0.05	0.00623	. . .	0.00620
$MnCl_2$	0.05	0.00617	0.00617	. . .

TABLE VII. TlCl in the presence of $MgCl_2$, $CaCl_2$, $BaCl_2$, $MnCl_2$, $ZnCl_2$, and $CuCl_2$.
(Continued)

Salt added.	Its Concentration.	Solubility of TlCl.	Mean of Experiments.	Mean for the six salts.
$MnCl_2$	0.05	0.00617	. . .	. . .
$ZnCl_2$	0.05	0.00627	0.00627	. . .
$ZnCl_2$	0.05	0.00627	. . .	. . .
$CuCl_2$	0.05	0.00613	0.00614	. . .
$CuCl_2$	0.05	0.00616	. . .	. . .
$MgCl_2$	0.1	0.00412	0.00413	. . .
$MgCl_2$	0.1	0.00413	. . .	. . .
$CaCl_2$	0.1	0.00416	0.00417	. . .
$CaCl_2$	0.1	0.00418	. . .	. . .
$BaCl_2$	0.1	0.00423	. . .	. . .
$BaCl_2$	0.1	0.00426	0.00425	. . .
$BaCl_2$	0.1	0.00426	. . .	0.00417
$MnCl_2$	0.1	0.00410	0.00412	. . .
$MnCl_2$	0.1	0.00413	. . .	. . .
$ZnCl_2$	0.1	0.00412	0.00412	. . .
$ZnCl_2$	0.1	0.00412	. . .	. . .
$CuCl_2$	0.1	0.00419	. . .	. . .
$CuCl_2$	0.1	0.00425	0.00422	. . .
$CuCl_2$	0.1	0.00422	. . .	. . .
$MgCl_2$	0.2	0.00273	0.00275	. . .
$MgCl_2$	0.2	0.00277	. . .	. . .
$CaCl_2$	0.2	0.00284	0.00284	. . .
$CaCl_2$	0.2	0.00284	. . .	. . .
$MnCl_2$	0.2	0.00287	0.00286	0.00283
$MnCl_2$	0.2	0.00284	. . .	. . .
$ZnCl_2$	0.2	0.00279	. . .	. . .
$ZnCl_2$	0.2	0.00279	0.00281	. . .
$ZnCl_2$	0.2	0.00286	. . .	. . .
$CuCl_2$	0.2	0.00291	0.00291	. . .
$CuCl_2$	0.2	0.00292	. . .	. . .

II. DISSOCIATION OF THE BIVALENT-METAL CHLORIDES.

The somewhat remarkable and unexpected conclusion may be drawn at once from these figures that all the chlorides here considered are very nearly equally dissociated. That, in spite of the rather large variations occurring in special cases, the effect of these different salts on the solubility is in reality essentially the same may be clearly seen from a close inspection of the results.

The mean value of the solubility for the six salts has therefore been used in the calculation of the dissociation by formula (5). The results are given in the following table:

TABLE VIII. Dissociation of $MgCl_2$, $CaCl_2$, $BaCl_2$, $MnCl_2$, $ZnCl_2$, and $CuCl_2$.

Concentration (y).	Dissociation ($100a_1$).	Constant $= \frac{1-a_1}{a_1^3 y^2}$
0.0347	82.2	267
0.0567	77.6	150
0.1045	69.4	83
0.2030	61.5	40

In all the cases previously considered the added salts have been binary, and the dissociation could take place only in one way. In the case of these bivalent-metal chlorides, however, two ways of dissociation are possible. Taking calcium chloride as an example, it is evident that this can break up, either into three ions, according to the reaction, $CaCl_2 = \overset{++}{Ca} + \overset{-}{Cl} + \overset{-}{Cl}$, or into two, according to the reaction, $CaCl_2 = \overset{+}{CaCl} + \overset{-}{Cl}$;[1] or partly in the one way and partly in the other.

This consideration is of importance; for without it the values of the above table are misleading. All that is determined by the solubility effect is the number of free chlorine ions in the solution of the added salt; and by the percentages given in the second column, headed "dissociation," is to be understood that the added salt gives rise to

[1] The dibasic organic acids have been shown by Ostwald (Zeitschrift für physikalische Chemie, 3, 282) to dissociate in this way; that is, only one hydrogen atom splits off until a very high dilution is reached.

that number of chlorine ions which it would give rise to if dissociated into *three* ions to the extent stated; the true dissociation is greater than this, if dissociation into two ions simultaneously takes place; but its value is not determined by these experiments.

The question whether the dissociation takes place in the one way or in the other, or in both at the same time, is one of considerable interest, and can be answered by determining whether the dissociation-values obtained at the four different concentrations vary in accordance with the laws of dissociation. It is clear, in the first place, since the dissociation exceeds fifty per cent., that the dissociation into two ions cannot alone take place; and it remains only to determine which of the two cases occurs, dissociation into three ions alone, or dissociation into three ions accompanied by that into two. In the former case the laws of mass action require that

$$\begin{matrix} Cy^3 a_1^3 = y\,(1 - a_1) \\ (Ca + Cl + Cl = CaCl_2) \end{matrix} \left[\text{ or } C = \frac{1 - a_1}{y^2 a_1^3} \right]$$

The values of this theoretical constant are given in the third column of the above table, and their variation is such that the assumption that a dissociation into three ions alone occurs is obviously untenable. The dissociation diminishes much too slowly with increasing concentration. The solutions of the chlorides RCl_2 probably contain, therefore, undissociated RCl_2 molecules, and three kinds of ions, namely: $\overset{++}{R}$, $\overset{-}{Cl}$, and $\overset{+}{RCl}$, and the last kind is present in considerable quantities in the more concentrated solutions.

Finally, concerning the degree of the dissociation, it may be remarked that it is not very different from that of the alkali chlorides; it is, however, a few per cent. less.

12. EXPERIMENTS WITH THALLOUS CHLORIDE AND CADMIUM CHLORIDE. DISSOCIATION OF THE LATTER.

Of the bivalent-metal chlorides which I investigated, all proved to be dissociated to practically the same extent, with the single exception of cadmium chloride. This was found to diminish the solubility of thallous chloride much less than the chlorides above considered. Its effect on the solubility is shown in the table upon the next page.

TABLE IX. TlCl in the presence of $CdCl_2$. Dissociation of $CdCl_2$.

Concentration (x).	Solubility of TlCl.	Mean.	Dissociation ($100\,a_1$).	Concentration (y).	Constant.
0	. . .	0.01612	. . .	. . .	. . .
0.025	0.01040	0.01040	59.7	0.0407	1140
0.025	0.01039	. . .	. . .	. . .	. . .
0.05	0.00780	0.00780	53.5	0.0628	773
0.05	0.00779	. . .	. . .	. . .	. . .
0.1	0.00576	0.00578	43.1	0.1111	577
0.1	0.00580	. . .	. . .	. . .	. . .
0.2	0.00429	0.00427	33.3	0.2098	410
0.2	0.00426	. . .	. . .	. . .	. . .

A comparison with the results of Table VII shows that a 0.2 normal solution of cadmium chloride reduces the solubility of thallous chloride to about the same extent as a 0.1 normal solution of the other bivalent-metal chlorides. Both contain, therefore, nearly the same number of chlorine ions; or the dissociation of cadmium chloride in 0.2 normal solution is approximately one half that of the other chlorides in 0.1 normal solution. With increasing dilution, however, the dissociation of the former increases much more rapidly than that of the latter, as was to be expected.

The figures of the last column of the above table, which are the values of the theoretical constant $\frac{1 - a_1}{a_1^3 y^2}$ corresponding to the dissociation into three ions, indicate that this manner of dissociation is not the only one, and it is highly probable that besides cadmium and chlorine ions, compound ions CdCl are also present in the solution.

Considering the many similarities between the elements cadmium and zinc, and their positions in the periodic system, it might well have been expected that zinc chloride would at least occupy an intermediate place between cadmium and the alkaline earth chlorides in respect to its dissociation. We have seen, however, that this was not the case, zinc chloride not differing appreciably in its solubility effect from the alkaline earth chlorides — a fact again established by the experiments with lead chloride described below.

I must not fail to mention that these conclusions concerning the

relative dissociation of the bivalent-metal chlorides are identical with those to which consideration of the electrical conductivity of their solutions leads. For example, according to the experiments of Kohlrausch[1] and Wershoven,[2] the ratio of the molecular conductivity of a 0.1 normal solution to that of an extremely dilute one is 0.75 in the case of barium chloride, 0.74 in that of zinc chloride, and 0.42 in that of cadmium chloride, thus practically identical in the first two cases and greatly less in the last.

Finally in this connection, let me call attention to the experiments of Tammann[3] on the diminution of the vapor pressure of water at 100° by these chlorides. The values of this in millimeters in the case of solutions containing one molecule of salt in two kilograms of water were as follows:

KCl	$BaCl_2$	$SrCl_2$	$CaCl_2$	$MgCl_2$	$ZnCl_2$	$CdCl_2$
12.2	16.4	16.8	17.0	16.8	9.2	9.6

While the solubility and conductivity experiments place beyond doubt the fact that zinc and the alkaline earth chlorides are nearly equally dissociated at ordinary temperatures, these results of Tammann seem to justify the interesting conclusion that at the boiling temperature the degrees of dissociation of zinc and *cadmium* chlorides are equal. Solubility experiments with these chlorides at higher temperatures would therefore be of great interest.

13. EXPERIMENTS WITH THALLOUS CHLORIDE AND MERCURIC AND LEAD CHLORIDES.

As mercuric chloride is known from its feeble conductivity to be very little dissociated, its effect on the solubility of thallous chloride might be expected to be nearly inappreciable. But the great tendency of this compound to form double salts manifests itself in this case also, and makes the principles of solubility effect inapplicable. When a solution of mercuric chloride is added to one of thallous chloride, a leafy white precipitate immediately forms, which has been shown by Jörgensen[4] to have the composition $HgCl_2$, $TlCl$.

As I intended to try the effect of the various chlorides on the solubility of lead chloride, the effect of this last on that of thallous

[1] Annalen der Physik und Chemie, **26**, 195.
[2] Zeitschrift für physikali-che Chemie, **5**, 495, 507.
[3] Zeitschrift für physikalische Chemie, **2**, 42.
[4] Journal für praktische Chemie, (2) **6**, 86.

chloride was of especial importance. Experiments to determine this were repeatedly tried with utterly discordant results. This led to an investigation of the precipitate formed by the addition of lead chloride to a solution of thallous chloride, and this precipitate was found to consist not of the latter alone, but of a double salt of the two. The salt, which separated in thin pearly scales, was recrystallized from a half saturated solution of lead chloride, in order to free it from excess of thallous chloride, and then from hot water. It is but very little soluble in cold water, but more readily in hot. It gave on analysis results as follows:

	Found.	Calculated for $PbCl_2$, 3TlCl.
Pb	21.78	20.76
Tl	60.15	61.46
Cl	17.96	17.78
	99.89	100.00

Its composition corresponds most closely to the formula $PbCl_2$, 3TlCl. The salt was apparently not pure, though recrystallization did not appreciably change the percentage of chlorine. As for my present purpose it was of importance only to prove the existence of a double salt, in order to explain the anomaly in the solubility effect, I did not further follow the study of its composition. This example illustrates the second above-mentioned (page 261) cause of inapplicability of the principles of solubility effect, and shows, conversely, how an anomaly in the latter may lead to the discovery of new double salts.

14. EXPERIMENTS WITH LEAD CHLORIDE AND POTASSIUM, MAGNESIUM, CALCIUM, MANGANESE, ZINC, AND CADMIUM CHLORIDES, AND HYDROCHLORIC ACID.

In order to confirm the values of the dissociation arrived at above, and to eliminate any error that might arise in individual cases from the occurrence of special chemical action between the dissolved substances, such as we have just seen to occur between lead and thallous chloride, an entirely independent series of experiments was made, in which the effect of some of the same chlorides on another difficultly soluble chloride, namely that of lead, was investigated.

The saturation of the solutions was effected in the same manner as with thallous chloride. The amount of lead dissolved was determined volumetrically by adding an excess of standard potassium

bichromate, filtering, and, after addition of potassium iodide and sulphuric acid, titrating back with sodium thiosulphate with the aid of carbon bisulphide as indicator. The method gave excellent results.

The following table contains the results of these experiments:

TABLE X. $PbCl_2$ in the presence of HCl, KCl, $MgCl_2$, $CaCl_2$, $MnCl_2$, $ZnCl_2$, and $CdCl_2$.

Salt added.	Its Concentration.	Solubility of $PbCl_2$.	Mean of Experiments.
None.	0	0.07773	. . .
None.	. . .	0.07771	. . .
None.	. . .	0.07765	0.07770
None.	. . .	0.07773	. . .
None.	. . .	0.07767	. . .
HCl.	0.05	0.04786	0.04786
HCl.	0.05	0 04786	. . .
HCl.	0.1	0.03244	0.03243
HCl.	0.1	0.03242	. . .
HCl.	0.2	0.01923	0.01927
HCl.	0.2	0.01932	. . .
KCl.	0.05	0.0480	. . .
KCl.	0.05	0.0481	0.0482
KCl.	0.05	0.0487	. . .
KCl.	0.1	0.0341	0.0341
KCl.	0.1	0.0342	. . .
KCl.	0.2	0.0218	. . .
KCl.	0.2	0.0219	0.0219
KCl.	0.2	0.0220	. . .
$MgCl_2$.	0.05	0.0503	0.0503
$MgCl_2$.	0.05	0.0503	. . .
$MgCl_2$.	0.1	0.0350	0.0350
$MgCl_2$.	0.1	0.0350	. . .
$CaCl_2$.	0.05	0.0499	. . .
$CaCl_2$.	0.05	0.0503	0.0503
$CaCl_2$.	0.05	0.0506	. . .
$CaCl_2$.	0.1	0.0354	0.0355

TABLE X. $PbCl_2$ in the presence of HCl, KCl, $MgCl_2$, $CaCl_2$, $MnCl_2$, $ZnCl_2$, and $CdCl_2$.
(Continued)

Salt added.	Its Concentration.	Solubility of $PbCl_2$.	Mean of Experiments.
$CaCl_2$.	0.1	0.0357	. . .
$CaCl_2$.	0.2	0.0218	. . .
$CaCl_2$.	0.2	0.0220	0.0219
$CaCl_2$.	0.2	0.0220	. . .
$MnCl_2$.	0.05	0.0501	0.0501
$MnCl_2$.	0.05	0.0500	. . .
$MnCl_2$.	0.1	0.0347	. . .
$MnCl_2$.	0.1	0.0349	0.0349
$MnCl_2$.	0.1	0.0349	. . .
$MnCl_2$.	0.2	0.0217	. . .
$MnCl_2$.	0.2	0.0217	0.0217
$MnCl_2$.	0.2	0.0218	. . .
$ZnCl_2$.	0.2	0.0220	0.0220
$ZnCl_2$.	0.2	0.0220	. . .
$CdCl_2$.	0.05	0.0600	0.0601
$CdCl_2$.	0.05	0.0603	. . .
$CdCl_2$.	0.1	0.0480	0.0481
$CdCl_2$.	0.1	0.0482	. . .
$CdCl_2$.	0.2	0.0355	0.0355
$CdCl_2$.	0.2	0.0355	. . .

A consideration of these results gives rise to the following conclusions:

1. The four chlorides of magnesium, calcium, manganese, and zinc, exert practically the same effect on the solubility of lead chloride.

2. Potassium chloride reduces its solubility to a slightly greater extent than the bivalent-metal chlorides just mentioned.[1]

3. Hydrochloric acid diminishes its solubility to a somewhat greater extent than potassium chloride.

[1] Except in the case of the most concentrated solution (0.2 normal), where it reduces it by the same amount.

4. A 0.2 normal cadmium chloride solution dissolves the same quantity of lead chloride as a 0.1 normal solution of the other bivalent-metal chlorides.

Each of these statements has been shown above[1] to hold true in the case of thallous chloride, so that in every particular the relative influence of the various chlorides on the solubility of thallous and lead chlorides is the same. This result is an evident consequence of the theory of solubilty effect, and it greatly confirms the conclusions above drawn in regard to the dissociation of the chlorides. For if in a particular case any disturbing cause, like the formation of a double salt, made the principles of solubility effect inapplicable, it is improbable that that same cause would exist, and especially so that it would exert the same influence, in the case of two dissimilar substances like lead and thallous chloride. If, for example, the fact that a 0.2 normal solution of cadmium chloride exerts the same influence as a 0.1 normal solution of calcium chloride on the solubility of thallous chloride is due not to the smaller dissociation of the former, but to the formation of a double salt between it and thallous chloride, then the behavior of cadmium and calcium chlorides towards lead chloride can be explained only by assuming likewise the formation of a double salt between lead and cadmium chlorides; and it is, moreover, necessary to assume its formation in quantity just sufficient to produce the strange coincidence in question — an occurrence so improbable as to be scarcely worthy of consideration.

It is possible, however, in the case of the bivalent-metal chlorides to show quantitatively that the experiments with lead chloride lead to nearly the same values of the dissociation as those with thallous chloride. This I will now proceed to do, in the converse manner, however, by showing that the solubility of lead chloride calculated from the values of the dissociation deduced from the thallous chloride experiments agrees with that found experimentally.

15. THEORY OF SOLUBILITY EFFECT BETWEEN TWO TERNARY ELECTROLYTES.

Up to the present time no attempt has been made to extend the principles of solubility effect to the case where the substance with which the solution is saturated breaks up into three ions. Therefore, although the experiments contained in the foregoing table were made with the special purpose of confirming the dissociation values obtained

[1] Pages 278, 279, 273, and 280.

with thallous chloride, it has been thought best in what follows to make use of them as examples of the theory of solubility.

In the attempt to calculate the solubility of lead chloride in the presence of other chlorides, two difficulties are met with. First, we have no direct knowledge of the dissociation of lead chloride. As stated above, I had hoped to determine this by studying its influence on the solubility of thallous chloride; but this failed, owing to the formation of a double salt between them. We are helped out of this difficulty, however, by the fact above shown, that all the investigated bivalent-metal chlorides, with the single exception of that of cadmium, are equally dissociated, so that it is highly probable that lead chloride agrees with them in this respect. The second difficulty is more serious, and arises from the above demonstrated probability that the bivalent-metal chlorides dissociate in two ways, both into two ions and into three; lead chloride, for example, on the one hand, into $\overset{+}{PbCl}$ and $\overset{-}{Cl}$, and on the other into $\overset{++}{Pb}$, $\overset{-}{Cl}$ and $\overset{-}{Cl}$. As long, however, as the solutions are not too concentrated, the quantity of PbCl ions cannot be large, and a tolerably good agreement with the facts may be expected from the assumption that the dissociation into three ions alone takes place.

The condition of equilibrium existing between lead chloride and its dissociation products is represented by the following equation, in which the symbols stand for the active masses of the substances represented by them, and C_1 and C_2 are dissociation constants:

$$PbCl_2 = C_1 \times \overset{++}{Pb} \times \overset{-}{Cl} \times \overset{-}{Cl} + C_2 \times \overset{+}{PbCl} \times \overset{-}{Cl}.$$

By the fundamental principle of solubility effect the amount of undissociated lead chloride in the saturated solution is invariable, whatever other salt may be simultaneously present. The right hand member of the equation must, therefore, also be a constant quantity. This member becomes now much simplified from the relation required by the laws of mass action,

$$\overset{+}{PbCl} = C_3 \times \overset{++}{Pb} \times \overset{-}{Cl},$$

which holds true since the amount of undissociated $PbCl_2$ is constant.[1] It follows, therefore, that

$$\overset{++}{Pb} \times \overset{-}{Cl} \times \overset{-}{Cl} = \text{a constant.}$$

That is to say, even under the assumption that the dissociation takes

[1] Otherwise the quantity of $\overset{+}{PbCl}$ would be a function of that as well.

place in both possible ways, it is nevertheless strictly true that the product of the active mass of the lead ions into the square of the active mass of the chlorine ions is a constant quantity. Difficulty arises, however, in the practical application of this principle, if we admit the existence of PbCl ions; for in that case we have no means of knowing the quantity of lead ions present in the saturated solution of lead chloride in pure water. But if we assume that the number of lead ions is one half the number of the chlorine ions, the quantity of which has been shown by the experiments with thallous chloride, all necessary data become known.

Under that assumption, the constancy of the product of the active masses of the lead and chlorine ions is expressed in the case that the added salt is also ternary by the formula,

$$m_0^3 a_0^3 = ma\,(ma + xa_1)^2,$$

in which the letters have the same significance as before (see page 261). When the two salts are equally dissociated in equally concentrated solutions, $a = a_1$, and its value is that corresponding to the concentration $m + x$ of either salt alone, as may easily be shown in a manner similar to that on page 269. The above equation may then be written

$$m^3 + 2xm^2 + x^2 m - \left(\frac{m_0 a_0}{a}\right)^3 = 0.$$

This equation has evidently but one positive root. The algebraic solution is of no assistance in determining its value, but it is easily calculated in each special case by Horner's method, after substitution of the numerical values of x, m_0, a_0, and a. This formula should represent the effect of magnesium, calcium, zinc, and manganese chlorides on the solubility of lead chloride. The values of the dissociation a_0 and a used in calculating the theoretical solubility m were obtained by graphic interpolation from those of Table VIII. The full data are as follows:

$m_0 = 0.0777$; $a_0 = 0.733$: for $x = 0.05$, $a = 0.697$; for $x = 0.1$, $a = 0.661$; and for $x = 0.2$, $a = 0.605$.

These calculated solubilities are placed in the following table by the side of the mean values of the results experimentally obtained with the chlorides of magnesium, calcium, zinc, and manganese.

TABLE XI. Calculated and actual solubility of $PbCl_2$ in presence of $MgCl_2$, $CaCl_2$, $ZnCl_2$, and $MnCl_2$.

Added Quantity (x).	Actual Solubility.	Calculated Solubility.
0.00	0.0777	. . .
0.05	0.0502	0.0522
0.10	0.0351	0.0351
0.20	0.0218	0.0176

In the case of the two diluter solutions, the agreement between the theoretical and experimental values is quite satisfactory; in the case of the most concentrated one, the divergence is, as was to be expected, somewhat larger. These results deserve consideration, I think, not only for their bearing on the phenomena of solubility, but also as an extension of the principles of mass action to a case of dissociation not previously studied. One example of dissociation into three components has indeed been given by Naumann and Horstmann, namely, that of ammonium carbamate into ammonia (2 mols.) and carbonic dioxide. This was, however, a condition of equilibrium between a solid body and its dissociation products, and not one in a homogeneous system between the undissociated and dissociated portions of a compound.

In the case of the other chlorides whose effect on the solubility of lead chloride was tried, namely, cadmium and potassium chlorides and hydrochloric acid, the calculation of the solubility becomes very complicated; for the assumption that the added salt and that with which the solution is saturated are equally dissociated no longer holds. Even if practicable, this calculation would be hardly necessary; for, a pretty close agreement between theory and fact having been shown to exist in the case of the chlorides of magnesium, calcium, zinc, and manganese, it follows from the facts discussed on page 284, that the same must hold true in the case of the other chlorides.

16. EXPERIMENTS WITH LEAD CHLORIDE AND MERCURIC CHLORIDE AND LEAD NITRATE.

As lead chloride is one of the few bivalent-metal chlorides with which mercuric chloride has not been shown to form a double salt, I thought that possibly one did not exist, and that the effect of mercuric

chloride on the solubility of lead chloride might be in accordance with the principles of solubility effect. The experiments proved, however, that such was not the case; for a considerable increase in the solubility took place, indicating the existence of a soluble double compound.

Lead nitrate, whose effect on lead chloride was studied with the idea of obtaining some information concerning the number of free lead ions in its solution, was found to act in the same way, causing an increased instead of a diminished solubility.

The results of two experiments made with these substances are given in the following table:

TABLE XII. $PbCl_2$ in the presence of $HgCl_2$ and $Pb(NO_3)_2$.

Salt added.	Its Concentration.	Solubility of $PbCl_2$.	Mean Solubility.
None.	0	0.0777	0.0777
$HgCl_2$	0.1	0.0997	0.0992
$HgCl_2$	0.1	0.0987	. . .
$Pb(NO_3)_2$	0.2	0.0824	0.0832
$Pb(NO_3)_2$	0.2	0.0841	. . .

17. CONCLUSION.

It seems desirable at the close of this somewhat lengthy article to recapitulate the more important results contained in it. The investigation was undertaken with the general purpose of showing that solubility experiments furnished us with a new and quite accurate method of determining the dissociation of salts, and with the special purpose of applying this method in order to obtain information concerning the dissociation of the chlorides of the various elements.

The effect of eleven different chlorides on the solubility of thallous chloride was investigated, each in four distinct concentrations, and the dissociation of each was calculated by means of the principles of solubility effect. The three alkali-metal chlorides, potassium, sodium, and ammonium, were found to be equally dissociated, their dissociation increasing from sixty-five per cent. at 0.2 to eighty-nine per cent. at 0.03 normal. Hydrochloric acid did not differ very greatly from these; it was, however, a little more dissociated, the values varying from seventy-three per cent. to eighty-nine per cent. between the

named concentrations. With a single exception all the bivalent-metal chlorides investigated, namely those of magnesium, calcium, barium, zinc, manganese, and copper, proved, like the univalent metal chlorides, to be equally dissociated — a rather remarkable fact when the dissimilarity of the elements is considered. Their dissociation is at all four concentrations about five per cent. less than that of the alkali chlorides. Cadmium chloride forms the exception spoken of; its dissociation is very much less than that of the other bivalent-metal chlorides, being at the four concentrations, in its case 33, 43, 53, and 60 per cent., while it is 62, 69, 78, and 82, in the case of the latter chlorides.

In confirmation of these results it was then shown that these different chlorides have the same relative effect on the solubility of lead chloride as on that of thallous chloride, thus eliminating the possible error that might arise in individual cases from the formation of double salts. And in the case of the bivalent-metal chlorides, the correctness of the dissociation values deduced from the thallous chloride experiments was proved almost conclusively by showing that the solubility of lead chloride was diminished to the extent corresponding to those values. The solubility of the lead chloride in the presence of the other chlorides was not calculated; but it follows from the fact just stated concerning the relative effect of the various chlorides that the two series of experiments (with thallous and lead chlorides) lead, in their case also, to practically the same values of the dissociation.

As the salts were investigated at four independent concentrations, it was possible to determine the manner in which the dissociation varies with the dilution; and one of the most important results arrived at is the proof that the univalent-metal chlorides follow the laws of dissociation in this respect. These laws are not followed, however, if the dissociation values deduced from the electrical conductivity are assumed correct; and this fact formed one of the few anomalies which the dissociation theory had not been able to explain. A comparison of the dissociation deduced from the solubility effect with that deduced from the electrical conductivity showed very considerable differences, especially in the case of the strong solutions. These experiments serve, therefore, to confirm the conclusion already drawn in my previous article that the electrical conductivity does not furnish an accurate measure of the dissociation except in cases where the number of ions present in the solution is very small, as in the case of weak organic acids.

The bivalent-metal chlorides were not found to obey the laws of mass action governing dissociation into three components, even approximately; and this led to the conclusion that dissociation into two ions, according to the reaction, $MCl_2 = \overset{+}{M}Cl + \overset{-}{Cl}$, probably accompanies that into three — a conclusion, however, of which further confirmation is desirable.

Finally, there should be mentioned the close agreement of the calculated with the actual solubility of lead chloride in the presence of other bivalent-metal chlorides; for in this calculation is involved an extension of the principles of mass action to a kind of dissociation not previously studied; and by it is contradicted what I believe to be a fundamental error in the statement of those principles. I refer, namely, to the so generally adopted statement of the law of Guldberg and Waage, that chemical action is proportional to the number of *equivalents* of each of the reacting substances in the unit of volume. Instead of "equivalents" should be inserted, I think, "molecules." The case above studied makes clear the fundamental difference between the two statements. The former would require that in a saturated solution of lead chloride the product of the number of equivalents of lead into the number of equivalents of chlorine be constant, while the latter requires that the product of the number of lead molecules into the *square* of the number of chlorine molecules be constant. This single example is by no means sufficient to establish the general principle, and it is very desirable to bring further experimental proof of it.

In conclusion, I desire to express my great obligation to my friend Dr. S. P. Mulliken, by whom many of these experiments were carried out.

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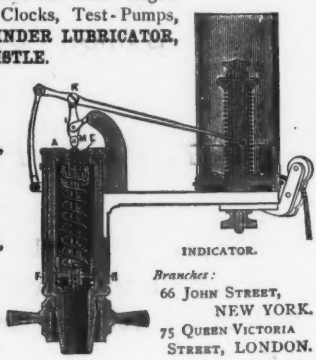

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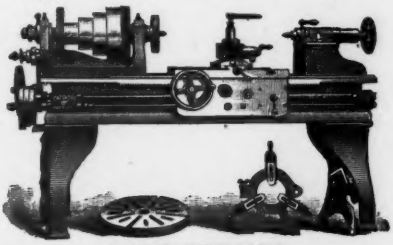

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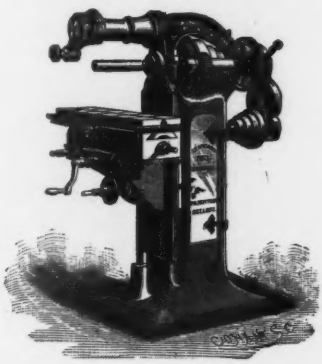

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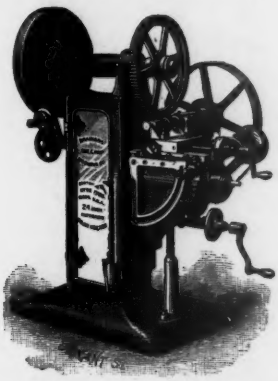

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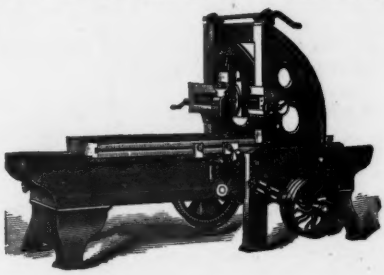

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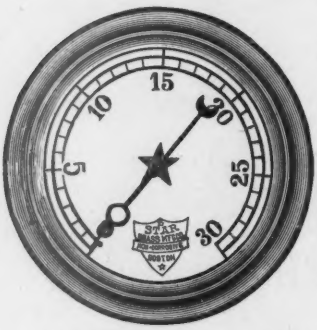

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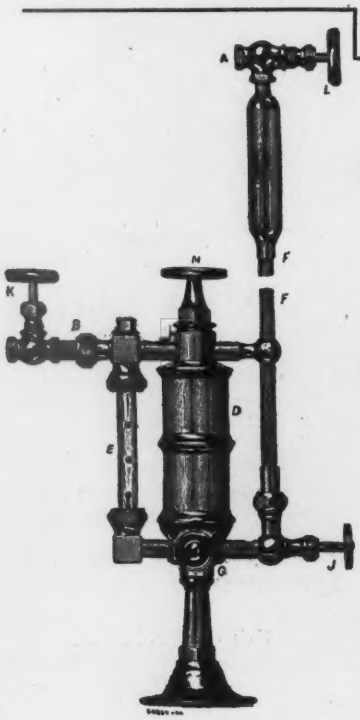

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